DIELECTRIC AND RELATED PHENOMENA

DRP'98

Abstracts

Szczyrk, Poland
24–27 September 1998

Technical University of Łódź
Branch in Bielsko–Biała
Textile Institute

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13. ABSTRACT (Maximum 200 words)

The Final Proceedings for Fifth International Conerence on Dielectric and Related Phenomena, 24 September 1998 - 27 September 1998

This is an interdisciplinary conference. Topics include: relaxation theory, characterization of dielectric responses, molecular dynamics, "smart" dielectric, polymer-ceramic structures, non-linear optical materials, space charges in dielectric, dielectric relation phenomena in polymers, liquid crystal polymers, liquid crystals, biological and pharmaceutical materials, aging of insulators, vacuum breakdown, man-made fibers, new experimental techniques, dielectric monitoring of chemical reactions.

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V-th International Conference on

DIELECTRIC AND RELATED PHENOMENA DRP '98

PROGRAMME

24 - 27 September
Szczyrk, POLAND

Technical University of Łódź,
Branch in Bielsko - Biała
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<u>Wednesday</u> <u>*23th September 1998*</u>

from 12.00 - ***Registration in Hotel "WLOKNIARZ" in Szczyrk, Willowa street 12 (on 24th Sept. the registration desk will be moved to nearby hotel „Zagron", Wrzosowa street 21)***

20.00 - ***Informal get-together reception***

<u>Thursday</u> <u>*24th September 1998*</u>

7.40 - 8.40 ***Breakfast***

8.40 - 9.00 ***Opening of the Conference***

Session 1 - Chairman M. Kryszewski

9.00 - 9.40	**Friedrich KREMER**	"Molecular dynamics close to (lubricated) surfaces"
9.40 - 10.20	**Thierry DITCHI**	"Study of space charge dynamics in solid dielectrics by simultaneous measurements of external current and space charge distributions"
10.20 - 10.40	**Erwin LEPOUDRE**	"Study of inverted micelles by linear and nonlinear dielectric spectroscopy"

10.40 - 11.10 ***Coffee break***

Session 2 - Chairman J. Ulanski

11.10 - 11.50	**Andrew JONSCHER**	"Physics of low-loss dielectrics"
11.50 - 12.30	**Maria MASSALSKA-ARODZ**	"Correlations in systems of complex dynamics"

13.00 - 15.00 ***Lunch***

Session 3 - Chairman L. Brehmer

15.00 - 15.40	**Marian KRYSZEWSKI**	"Relation between structure and electrical properties of diamond and diamond-like structures"
15.40 - 16.00	**Igor VRAGOVICH**	"Dielectrical properties of thin molecular film–structures"
16.00 - 16.20	**Sergei FEDOSOV**	"Isothermal and non–isothermal relaxation in dye–doped polystyrene"
16.20 - 16.40	**Stanislaw A. ROZANSKI**	"Dielectric spectroscopy of confined smectic liquid crystal phases"

16.40 - 17.10 ***Coffee break***

Session 4 - Chairman S. Bauer

17.10 - 17.50	**Bozena HILCZER**	"Structural relaxation in some superprotonic conductors"
17.50 - 18.10	**M. STOCKHAUSEN**	"Dielectric spectroscopy of some electrolyte solution in dimethylsulfoxide/water mixtures"
18.10 - 18.30	**Kenji OKAMOTO**	"Observation of the copper ionic migration in the insulation layer by a pulsed electroacoustic method"

19.00 - 20.00 ***Dinner***

20.30 - 22.30 ***Round-table Discussion***

<u>Friday</u> *<u>25th September 1998</u>*

7.40 - 8.40	***Breakfast***		
		Session 5 - Chairman F. Kremer	
8.40 - 9.20	Yuri FELDMAN	"Dielectric relaxation in complex systems"	
9.20 - 10.00	Jerzy MALECKI	"A model of long time decay of space charge in polymers"	
10.00 - 10.20	Ludwig BREHMER	"Space charge dynamics in disordered dielectrics"	
10.20 - 10.40	Henryk SODOLSKI	"Silica xerogel investigated by the method of thermally stimulated currents"	
10.40 - 11.10	***Coffee break***		
		Session 6 - Chairman T. Pakula	
11.10 - 11.50	Karina WERON	"Relaxation of complex systems. From local randomness to global determinism"	
11.50 - 12.30	Andrzej PLONKA	"Dispersive rate processes in condensed media"	
12.30 - 12.50	Zbigniew DENDZIK	"On the scaling of relaxational processes"	
13.00 - 15.00	***Lunch***		
		Session 7 - Chairman S. Gubanski	
15.00 - 15.40	Lucjan SOBCZYK	"Structure and dielectric behaviour of alkylammonium halogenoantimonates(III) and bismuthates(III)"	
15.40 - 16.00	Grzegorz BAK	"Decay of free electron–hole pairs in diamond–like carbon thin films"	
16.00 - 16.20	Jan PETZELT	"High–frequency dielectric spectroscopy of some high permittivity microwave ceramics"	
16.20 - 16.40	Jaroslaw RYBICKI	"The influence of excluded volume on transient currents in thin dielectric layers"	
16.40 - 17.10	***Coffee break***		
		Session 8 - Chairman P. Rolla	
17.10 - 17.50	Fabrizio PARODI	"Microwave heating and the acceleration of polymerization processes"	
17.50 - 18.10	S. COREZZI	"The check of the Stokes-Einstein-Debye diffusion law in epoxies of increasing molecular complexity"	
18.10 - 18.30	Krzysztof FRIEDRICH	"Isothermal curing of epoxy resins as seen by dielectric, direct–current and time–of–flight measurements"	
18.30 - 18.50	Daniele FIORETTO	"Dielectric and light scattering analysis of main and secondary relaxation dynamics"	
20.30 -	***Conference dinner***		

Saturday **26th September 1998**

7.40 - 8.40	***Breakfast***	
		Session 9 - Chairman J. Jadzyn
8.40 - 9.20	**Francois KAJZAR**	"Highly orientable side chain liquid crystalline polymers for quadratic nonlinear optics"
9.20 - 10.00	**Michael WÜBBENHORST**	"Dielectric relaxation in side-chain LC polymers"
10.00 - 10.20	**Antoni KOCOT**	"Dynamics of the AFLC molecules observed by dielectric, electro-optical response and time-resolved FTIR spectroscopy"
10.20 - 10.40	**Lidia OKRASA**	"Molecular dynamics in anisotropic composites based on LC cellulose derivatives"
10.40 - 11.10	***Coffee break***	
		Session 10 - Chairman O. Shpotyuk
11.10 - 11.50	**Juliusz SWORAKOWSKI**	"Dipolar species in molecular materials as charge carrier traps"
11.50 - 12.30	**Reimund GERHARD-MULTHAUPT**	"High space-charge densities in polar and non-polar dielectrics"
12.30 - 12.50	**Stanislav NEŠPŮREK**	"Metastable electronic states in poly(methyl phenylsilylene)"
13.00 - 15.00	***Lunch***	
		Session11 - Chairman A. Konsta
15.00 - 15.40	**Gisèle BOITEUX**	"Molecular dynamics of poly(ethylene 2,6 naphthalene dicarboxylate) (PEN) by dielectric spectroscopy"
15.40 - 16.20	**Aleksander SZYMANSKI**	"Time-domain investigations of organic materials"
16.20 - 16.40	**Dave PEARSON**	"Low frequency dielectric properties of pharmaceutical materials"
16.40 - 17.10	***Coffee break***	
		Session 12 - Chairman S. Fujita
17.10 - 17.50	**Gary. C. STEVENS**	"Scanning probe microscopy in the study of dielectrics"
17.50 - 18.30	**Alex GRISHIN**	"Epitaxial complex oxide heterostructures: processing, characterization and applications"
18.30 - 18.50	**Stefan LÁNYI**	"Low-frequency scanning capacitance microscopy"
19.00 - 20.00	***Dinner***	
20.30 - 22.30	***Poster session***	

Sunday *27th September 1998*

8.00 - 9.00	***Breakfast***		
		Session 13 - Chairman G. Seytre	
9.00 - 9.20		**Siegfried BAUER**	"Pulsed electrothermal technique for the characterization of dielectric films"
9.20 - 9.40		**L. IBOS**	"Thermal ageing of pyroelectricity in PVDF and P(VDF–TrFE) copolymers"
9.40 - 10.00		**Ivan RYCHETSKY**	"Dielectric properties of ferroelectric–metal microcomposites"
10.00 - 10.20		**Milada GLOGAROVÁ**	"Dielectric behavior of ferroelectric liquid crystals in the vicinity of the transition into the hexatic phase"
10.20 - 10.50	***Coffee break***		
		Session 14 - Chairman A. Włochowicz	
10.50 - 11.30		**A. S. SIGOV**	"Theoretical treatment of phase transition anomalies in dielectrics with static random disorder"
11.30 - 11.50		**Jan JADZYN**	"Dielectric relaxation of 6–CB dispersed in polymer matrix"
11.50 - 12.10	***Closing ceremony***		
12.30 - 13.30	***Lunch***		
Afternoon	***Excursion***		

P1.	**Tadeusz PAKULA**	"Simulation of dielectric relaxation effects in bulk polymers"
P2.	**Agnieszka JURLEWICZ**	"Relaxation phenomenon as a compound Bernoulli scheme"
P3.	**Krzysztof KOSMULSKI**	"Numerical investigations of relaxing fractal systems"
P4.	**Malgorzata KOTULSKA**	"A continuous time random walk model of the low frequency dispersion phenomenon in tissue"
P5.	**Vitaly PUSTOVIT**	"Numerical methods in calculations of electrodinamical properties of metallic composites"
P6.	**Fred ALBRECHT**	"Hopping transport in a disordered lattice simulation of dark discharge"
P7.	**Alexandra BUCHSTEINER**	"Investigation of optical switching of azothiols and azocontaining amphiphiles with dielectric spectroscopy"
P8.	**Peter FRÜBING**	"Diffrent molecular mechanisms for the dielectric hysteresis and the pyroelectricity in a poly(vinyl alkohol) with azobenzene–alkoxy side chains"
P9.	**Viktor BOVTUN**	"Simultaneous study of topography and local electrical properties of dielectrics : scanning capacitance, conductivity and surface charge microscopy"
P10.	**Viktor BOVTUN**	"Investigation and dielectric monitoring of crosslinking reaction in thermosets and elastomers with microwave methods"
P11.	**Enis Stanislaw M. TUNCER**	"Dielectric properties of composite structures with different two dimensional networks"
P12.	**Wojciech OTOWSKI**	"Effect of temperature and time on the complex permittivity of an insulating material"
P13.	**Shigetaka FUJITA**	"Electrical properties of polyimide"
P14.	**Simona BAUER–GOGONEA**	"Dielectric dilatometry on thin teflon–PTFE films prepared by pulsed–laser deposition"
P15.	**Oleg POZNANSKY**	"High–frequency dielectric dependencies of polymer materials"
P16.	**A. KLINSKIKH**	"Density of states a conformon in the disorder polymeric crystal"
P17.	**A. KLINSKIKH**	"The influence of conformational defects on optical absorption in a polysilane"
P18.	**Inta MUZIKANTE**	"Physical properties of thin evaporated films of indandione–1,3 pyridinium betaine and it derivatives"
P19.	**Yuri GOROKHOVATSKY**	"Thermally stimulated depolarization currents in low density polyethilene films"
P20.	**Natalia CORREIA**	"Physical aging on meta–toluidine studied by thermally stimulated depolarisation currents"
P21.	**Cristina ALVAREZ SANCHO**	"Influence of molecular weight in the thermally stimulated currents spectrum of a side–chain liquid crystalline polymer"
P22.	**Margarita GINOWSKA**	"Electrooptical investigation of nematic liquid crystals"
P23.	**Andrzej BAK**	"Investigations of dynamics of n-p-(ethoxybenzylidene) p'-propylaniline (EBPA)"
P24.	**J. KASPERCZYK**	"Phonon contribution to electroopitces coefficients in doped LNB single crystals"
P25.	**Maria MUCHA**	"Electrooptical effect in PDLC complex system prepared by solution cast method"
P26.	**Maria MUCHA**	"Dielectric relaxation phenomena in side chain liquid crystalline polycarbosilane of various spacer lengths"
P27.	**Adam BURCZYK**	"Dielectric relaxation in a system with the reentrant nematic phase"

DRP'98 Poster session (Saturday, 26th September 1998, 20.30 - 22.30)

P28.	**Grzegorz CZECHOWSKI**	"Dielectric relaxation of trioctylmethylammonium chloride"
P29.	**Slawomir CZERKAS**	"Static and dynamic dielectric properties of n–hexyloxy– and n–octyloxy– cyanobiphenyls"
P30.	**Przemyslaw KEDZIORA**	"Nonlinear dielectric relaxation in dipolar systems"
P31.	**Faustyna GOC**	"Dielectric properties of antiferroelectric liquid–crystalline mixtures"
P32.	**W. KUCZYNSKI**	"Switching behaviour of antiferroelectric liquid–crystalline mixtures"
P33.	**Boguslaw ZYWUCKI**	"Dipole-dipole correlation and odd-even effect in homologous series of bicyclo-[2,2,2]octanes derivatives with -NCS terminal groups"
P34.	**Boguslaw ZYWUCKI**	"Determination of the splay and bend Elastic Constants for thin nematic planar layer in external electric field"
P35.	**Mickola I. GRITSENKO**	"Influence of space charge on liquid crystal director dynamic"
P36.	**A.P. SITNIKOV**	"Relaxation processes in deformed liquid crystal layers"
P37.	**Pawel JANIK**	"Apparatus for dielectric relaxations measurements in low frequency range"
P38.	**G. PASTERNA**	"Dielectric relaxation of the Igepal in the planar and homeotropic geometries"
P39.	**M. GORNY**	"Dielectric relaxation and optical response of FLC samples in ferroelectric phase"
P40.	**Piotr HABDAS**	"Temperature and pressure studies of dielectric permittivity in the nitrobenzene–n–alkanes binary mixtures"
P41.	**Sylwester RZOSKA**	"Critical dynamics in the isotropic phase of nematogens and solution of limited miscinility tested by nonlinear dielectric effect measurements"
P42.	**Sylwester RZOSKA**	"Temperature and pressure studies of"linear" and"non–linear" dielectric relaxation in an epoxy resin"
P43.	**Pierangelo A. ROLLA**	"Splitting between main and secondary relaxations in mono-, di-, and tri-epoxy compounds"
P44.	**Gerard SEYTRE**	"In–situ electrical analysis in view of monitoring the processing of thermoplastics"
P45.	**Aleksander B. SZYMANSKI**	"Epoxide crosslinking studies by means of recording of electrode current"
P46.	**Agata BLAHUT**	"Low frequency electrical properties of non–crosslinked epoxide materials"
P47.	**Wiktor SZYMANSKI**	"On interfacial effects in nematic liquid crystals"
P48.	**Elzbieta SZWAJCZAK**	"On electrical conductivity of liquid–crystalline materials. Old results in light of new findings"
P49.	**Andrzej WASILEWSKI**	"Testing of mechanical properties of materials by means of optical method"
P50.	**Marek WOJCIECHOWSKI**	"Dielectric properties of liquid crystalline S–MHPOBC in the range of low–frequencies"
P51.	**Grzegorz BAK**	"Detection of structural inhomogeneity in graded index polymer materials by space charge measurements : numerical solutions"
P52.	**Elzbieta STARYGA**	"Electrical properties of some plasma polymers obtained by remote microwave plasma chemical vapour deposition"
P53.	**Maciej DLUZNIEWSKI**	"Electrical properties of DLC films in the metal/DLC/silicon heterostructures"
P54.	**Piotr STEPNIK**	"Discharge in dispersive systems under open–circuit conditions : computer simulation"
P55.	**Joanna SWIATEK-PROKOP**	"Dielectric properties of polyethylene modified by monoesters of maleic acid"

P56.	**Andrey K. KADASHCHUK**	"Thermoluminescence study of poly(methyl-phenylsilylene)"
P57.	**Leonas VALKUNAS**	"Charge separation and recombination in sensitized photoconducting polymers"
P58.	**Arkadiusz MANDOWSKI**	"Trapping and recombination kinetics in spatially correlated systems"
P59.	**Gilbert TEYSSEDRE**	"Tunnelling-mediated recombination-induced luminescence in polyethylene naphthalate"
P60.	**Jerome MENEGOTTO**	"Molecular motions in PVDF : a combined thermostimulated current and dielectric relaxation study"
P61.	**Sergei FEDOSOV**	"Space charge and polarization dynamics in PVDF and P(VDF-TFE)"
P62.	**Sergei FEDOSOV**	"Formation and relaxation of space charge in corona poled polystyrene"
P63.	**A. E. SERGEEVA**	"Dielectric relaxation in PVDF-$BaTiO_3$ Polymer-ceramic structures"
P64.	**A. E. SERGEEVA**	"Corona poling of a ferroelectric polymer (PVDF)"
P65.	**Marian OLSZOWY**	"Pyroelectricity in PVDF/PZT ceramic composites of 0-3 connectivity"
P66.	**Vasile TURA**	"Circuit influence on polarization reversal in $BaTiO_3$ ceramics"
P67.	**L. MITOSERIU**	"Analysis of the nonlinear circuits with ferroelectric capacitor in the frame of Landau-Devonshire theory"
P68.	**L. MITOSERIU**	"Grain size dependence of the dielectric properties in barium titanate ceramics"
P69.	**Leonid GRIN**	"Eu and Tm doped lithium tetraborate (LTB) crystals as material for thermoluminescence dosimeters"
P70.	**A.N. SHEKHOVTSOV**	"The thermo- and x-ray luminescence of $LaMgB_5O_{10}$ glasses doped by (Ce, Gd, Pr, Eu)"
P71.	**I. HRUBA**	"Infrared and raman spectroscopy of single crystal and textured glass ceramics of LaBGeO5"
P72.	**Ewa RYSIAKIEWICZ-PASEK**	"Study of polarisation and conductivity mechanism in photochromic glasses"
P73.	**Tadeusz WIKTORCZYK**	"Metal/insulator contacts in electrical examinations of $M/Yb_2O_3/M$ thin-film structures"
P74.	**Oleg SHPOTYUK**	"Dipol relaxation processes in electron-irradiated amorphous chalcogenide systems"
P75.	**Volodymyr P. BEREST**	"Conformational dynamic of fibrinogen by dielectric spectroscopy"
P76.	**Orest FL'UNT**	"Low-frequency dielectric properties of high-resistivity GaSe layered crystals"
P77.	**Victor ROZHKOV**	"Electrophysical properties of the switching MIS-structures with REE fluorides"
P78.	**Victor ROZHKOV**	"Antireflection and passivating coatings on the basis of Rare Earth element oxides for silicon devices"
P79.	**Alla TRUSOVA**	"Silicon MIS-structures with rare earth oxide films as insulator"
P80.	**Piotr GRYGIEL**	"On thermally stimulated currents under quasi-equilibrium transport regime"
P81.	**Wladyslaw TOMASZEWICZ**	"On determination of the trap distribution in disordered solids from the final decay of transient photocurrents"
P82.	**Jaroslaw RYBICKI**	"The influence of off-diagonal disorder on stationary current-field characteristics in hopping systems"
P83.	**Jaroslaw RYBICKI**	"Computer investigation of local order and long-range correlations in diluted random

		granular systems"
P84.	**Jaroslaw RYBICKI**	"Electric field dependence of transient currents profiles in spatially non–uniform dielectric layers"
P85.	**Grazyna JAROSZ**	"Photoconductivity of perylene layers"
P86.	**Leon MURAWSKI**	"Transport properties of glassy and crystallized Bi–Sr–Ca–Cu–O system"
P87.	**Przemyslaw ADAMSKI**	"Polarizability anisotropy of CB n molecules"
P88.	**Galina I. OVTCHINNIKOVA**	"Correlation between conductivity and dielectric spectra in hydrogen bound ferroelectrics"
P89.	**Larissa BRADOULINA**	"Dielectric relaxation of thin films based on PMMA and polyimide"
P90.	**Inna A. MALYSHKINA**	"Relation between structure and dielectric properties of hydrogels"
P91.	**Piotr URBANOWICZ**	"Molecular dipole moments determined from dielectric measurements in very diluted solutions"
P92.	**Bahadur SABUROV**	"The influence of X-ray irradiation on dielectric properties of thermotropic liquid crystals"
P93.	**Bahadur SABUROV**	"The influence of central bridge groups no the mechanism of dielectric polarization of liquid crystals"
P94.	**Pedro BRITO**	"Dielectric behavior of BiSrCaCuO sample"
P95.	**Pedro BRITO**	"Dielectric bahavior of lemon juice and model systems"
P96.	**Grzegorz BAK**	"Dielectric properties of mixtures of chitosan and diclofenac sodium"
P97.	**Galina V. POPOVA**	"Hexastar shape cyclotriphosphazenes as key substances for drug delivery"
P98.	**Maria JASTRZEBSKA**	"A fractal interpretation of the dielectric response of dopa–melanin biopolymer"
P99.	**Amalia A. KONSTA**	"Dielectric relaxation in cryoprotectants"
P100.	**Gamal Mohammed TURKY**	"Dielectric properties of bagasse and its constituents"
P101.	**Alexander KORHENKO**	„Investigations of the biopolymers by dielectric relaxation spectroscopy"
P102.	**Azima L.G. SAAD**	"Compatibility studies on some polymer blend systems by electrical and mechanical techniques"
P103.	**Augenie M. BISHAI**	"Electrical and mechanical properties of styrene–butadiene rubber reinforced with synthetic fiber"
P104.	**M.N. ISMAIL**	"The effect of the adhesion system (HRH) on the physico–mechanical and electrical properties of SBR/polyester short fiber composites"
P105.	**Ahmed M. GHONEIM**	"Dielectric and physico–mechanical properties of EPDM/NR blend loaded with different carbon blacks"

GENERAL INFORMATION

All session of the V-th International Conference will take place at the Hotel„ZAGROŃ" in Szczyrk near Bielsko-Biała.

The Conference Office

will be open from Thursday, 24th September at 7^{00}, throughout the Conference in Hotel „ZAGROŃ" Wrzosowa street 21, Szczyrk .

Registration

The registration desk, in the Hotel „WŁÓKNIARZ" in Szczyrk will be open on Wednesday, 23rd September 1998 at 12^{00}.

Registration includes admission to all scientific session, meeting materials, meals and accommodation.

Wednesday 23rd September 1998 - Informal get-together reception - 20^{00} pm at Hotel „WŁÓKNIARZ"

Meals

Only lunch will be served at the Hotel „ZAGROŃ" at 13^{00}.
Breakfast and supper will be served at Hotel „ZAGROŃ" and „WŁÓKNIARZ" suitable for your accommodation.

Breakfast	at	7^{40}
Supper	at	19^{00}

Coffee, tea and soft drinks will be served during the breaks of the scientific programme.

Social events

All participants are invited to the Conference Dinner on Friday, 25th September at 20^{30}.

Excursion

Sunday , 27th September after lunch - Oświęcim (former Nazi Concentration Camp in Auschwitz-Birkenau)

Sunday , 27th September after lunch - Site-tour through Beskid Moutains (Pętla Beskidzka)

V-th International Conference on

DIELECTRIC AND RELATED PHENOMENA
DRP'98

is organised by the:

Technical University of Łódź, Branch in Bielsko-Biała
Textile Institute Bielsko-Biała, Poland
in cooperattion with
Instytute of Polymers and Instytute of Physics
Technical University of Łódź, Poland

The Conference is organised under the honorary Chairmanship of
Mgr Andrzej Sikora
Voivode of Bielsko – Biała Province

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State Committee for Scientific Research (KBN)
Rector Technical University of Łódź
Stefan Batory's Foudation

Instruction for presentation

English is the working language of Conference. No translation will be provided. All materials for publication should be submitted in English.
The time for presentation (including discussion) will be : 40 minutes for invited lectures and 20 minutes for other oral contributions. Transparent foils and slides may be used to illustrate the lectures. A poster size is 0.9 m (width) x 1.2 m (height). Posters can be displayed during all the Conference.

Venue

Hotel **"WŁÓKNIARZ"**, Willowa street 12, 43-370 Szczyrk, Poland
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The registration desk, at Hotel "WŁÓKNIARZ" in Szczyrk, Willowa street 12, will be open from Wednesday, 23 September 1998 at 12:00.

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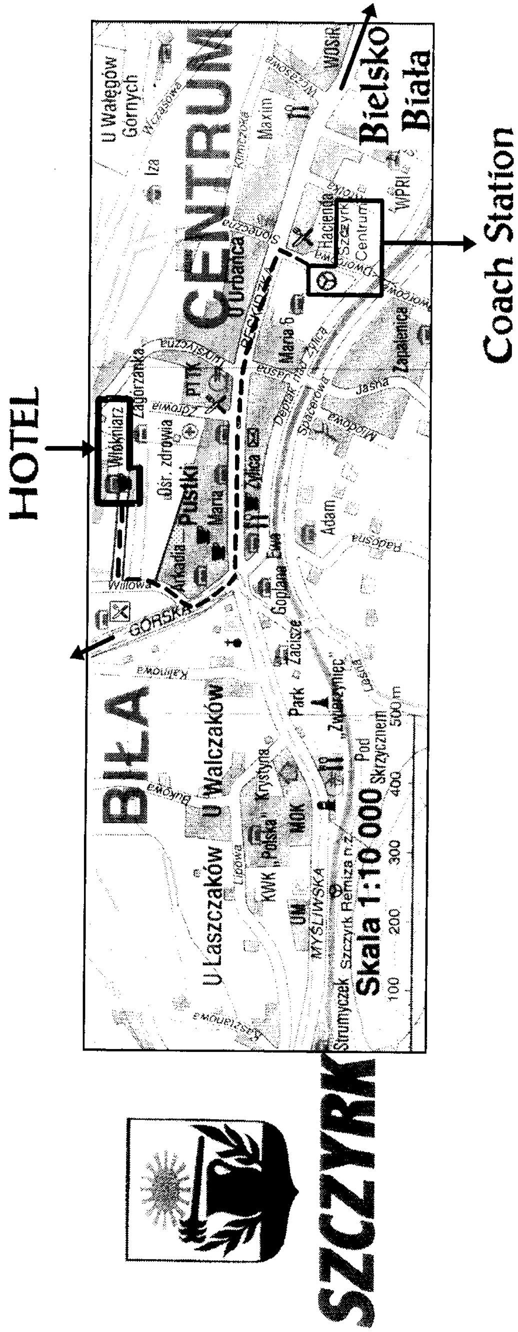

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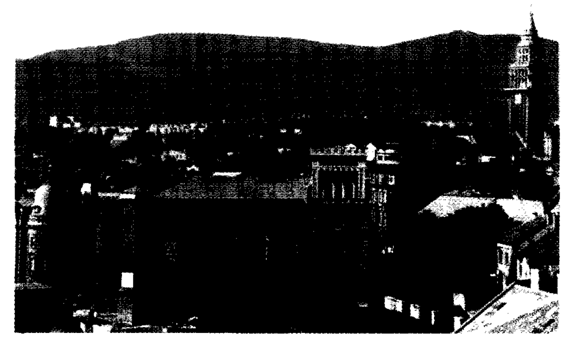
DRP'98

24 – 27 September 1998



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Third Circular

DRP'98

The 5 th International Conference of DRP'98 continues the tradition of a series of four international conferences on Dielectric and Related Phenomena, organised at intervals of two years in Poland. This conference is organised in Bielsko-Biała / Szczyrk for the second time.

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Program of the Conference

The following have agreed to give invited lectures:

- Claude ALQUIE, (Ecole Superieure de Physique et de Chimie Industrielles, Paris, France), *"Study of space charge dynamics in solid dielectrics by simultaneous measurements of external current and space charge distributions"*
- Gisele BOITEUX, (Universite "Claude Bernard" Lyon I, France) *"Molecular dynamics of poly(ethylene 2,6 dicarboxylate) (PEN) by dielectric spectroscopy"*
- Jean Claude DUBOIS, (THOMSON CSF, Orsay, France) *"Ferroelectric and pyroelectric polymers, properties and applications"*
- Yuri FELDMAN, (The Hebrew University of Jerusalem, Israel) *"Dielectric relaxation in complex systems"*
- Reimund GERHARD-MULTHAUPT, (Universitat Potsdam, Germany) *"High space-charge densities in polar and non-polar dielectrics"*
- Alex GRISHIN, (Royal Institute of Technology, Stockholm, Sweden) *"Epitaxial complex oxide heterostructures: processing, characterization and applications"*
- Bożena HILCZER, (Institute of Molecular Physics, Poznań, Poland). *"Structural relaxation in some superprotonic conductors"*
- Andrew JONSCHER, (University of London, Royal Holloway, Egham, UK) *"Physics of low-loss dielectrics"*
- Francois KAJZAR, (CEA, Gif sur Yvette, France) *"Highly orientable side chain liquid crystalline polymers for quadratic nonlinear optics"*
- Friedrich KREMER, (Universitat Leipzig, Germany) *"Molecular dynamics close to (lubricated) surfaces"*
- Marian KRYSZEWSKI, (Technical University of Łódź, Poland) *"Relation between structure and electrical properties of diamond and diamond like structures "*
- C. Le GRESSUS, (CEA, Monts, France) *"Space charge characterization for insulator specification"*
- Jerzy MAŁECKI, (Institute of Molecular Physics, Poznań, Poland) *"A Model of long time decay of space charge in polymers"*
- Maria MASSALSKA-ARODŹ, (Henryk Niewodniczanski Institute of Nuclear Physics, Kraków, Poland) *"Correlations in systems of complex dynamics"*
- Fabrizio PARODI, (SAIAG, Torino, Italy) *"Microwave heating and the acceleration of polymerization processes"*
- Andrzej PLONKA, (Technical University of Łódź, Poland) *"Dispersive rate processes in condensed media"*
- Ranko RICHERT, (Max-Planck-Institut fur Polymerforschung, Mainz, Germany) *"On the higher moments of dielectric polarisation"*
- A. S. SIGOV, (Technical University, Moscow, Russia) *"Theoretical treatment of phase transition anomalies in dielectrics with static random disorder"*
- Lucjan SOBCZYK, (University of Wroclaw, Poland) *"Structure and dielectric behaviour of alkylammonium halogenoantimonates (III) and bismuthates (III)"*
- Gary C. STEVENS, (University of Surrey, UK) *"Scanning probe microscopy in the study of dielectrics"*
- Juliusz SWORAKOWSKI, (Technical University of Wroclaw, Poland) *"Dipolar species in molecular materials as charge carrier traps"*
- Aleksander SZYMAŃSKI, (NIBR ELF, Poland) *"Time-domain investigations of organic materials"*
- Karina WERON, (Technical University of Wrocław, Poland) *"Relaxation of complex systems. From local randomness to global determinism"*
- Michael WUBBENHORST, (Delft University of Technology, The Netherlands) *"Dielectric relaxation in side-chain LC polymers"*

Detailed program of the conference will be available at the conference desk. At the end of August all invited speakers and the authors of papers selected for oral presentations will receive by e mail information about the time and day of their presentation.
We are planning seven oral sessions (two sessions every day: from 9 to 13 and from 15 to 19).
In the evenings:
Informal get-together reception on 23 Sept.
Conference Dinner – 24 Sept.
Round Table Discussion (and Beskid Folklore Show or Barbecue) – 25 Sept.
Poster Session – 26 Sept. (posters will be displayed from 24. Sept.)
Excursion – 27 Sept. (afternoon).

Abstracts and proceedings

All the submitted and accepted abstracts will be published in the Book of Abstracts which will be available at the Conference.
The Book of Proceedings containing all papers accepted and presented at the Conference will be edited by Polish Chapter of SPIE (The International Society for Optical Engineering, Bellingham, USA). The single author or the first one (if several) will receive a copy of the volume. We strongly request you to follow the below rules when preparing your papers :

- please use normal white sheets A-4 of good quality and prepare your manuscript (not more than 15 pages for invited lectures and 8 pages for all other papers) using a printer of good print quality (high contrast), preferably a laser print;
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  In this part you should avoid discussing other papers and present only your own achievements.
  The end part of the paper should be titled CONCLUSION(S) followed by ACKNOWLEDGEMENTS (if applicable) and REFERENCES. This titles should be preceded by the appropriate numbers. The number 1 always precedes the word INTRODUCTION, while the word ABSTRACT should be free of any number.
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CONTENTS

PLENARY LECTURES

ORAL PRESENTATION

STUDY OF SPACE CHARGE DYNAMICS IN SOLID DIELECTRICS BY SIMULTANEOUS MEASUREMENT OF EXTERNAL CURRENT AND SPACE CHARGE DISTRIBUTIONS

Claude Alquie
Laboratoire d'Electricité Générale, Ecole Supérieure de Physique et de Chimie Industrielles, Paris, France, e-mail: claude.alquie@espci.fr

Charge dynamics, transport phenomena and interfacial effects in dielectrics have been traditionally studied by various experimental techniques such as thermally stimulated currents, conduction current measurement or I(V) characeristics analysis. Another approach is now available due to the large development of non destructive methods for the measurement of electric field and space charge distributions.

In this presentation, we show how the siznultaneous measurement of the external current and of the charge distributions during polarisation and depolarisation periods brings a lot of new information on the charge dynamics. It makes possible to separate interfacial effects, such as injection at the electrode-insulator interface, from bulk conductivity effects and enables to compare experimental results with theoretical conduction and injection models.

First we recall the principles and techniques used to measure space charge distributions by the pressure wave propagation (PWP) method, and charging and discharging currents. We show what information can be obtained by each technique. Then we discuss brietly what can be expected from the combinaison of these two techniques.

An exparimental setup which allows for the simultaneous measurements of charge profiles by the PWP method and total external current during polarisation and discharge periods is described. It is applied to low density polyehylene plate samples having two semiconducting electrodes, made of the same materials as those involved in high voltage cables. The dynamics of the charges is studied at 20°C and 70°C.

The displacement and conduction currents can be determined everywhere in the sample, and particularly at the interfaces, in transient conditions. We present an experimental validatian of the zero field piane model. A quantitative treatment of the experimental data is perforrned in order to determine the injection characteristics of semiconductor-insulator contacts. It must be noticed that, in order to determine the whole injection characteristics at both interfaces, it is sufflcient to carry one experiment in transient conditions.

STRUCTURE AND DIELECTRIC BEHAVIOUR OF ALKYLAMMONIUM HALOGENOANTIMONATES(III) AND BISMUTHATES(III)

G. Bator, R. Jakubas and L. Sobczyk
Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50 383 Wrocław, Poland

Halo-coordinated Sb(III) and Bi(III) salts containing organic cations represent a rich family of crystals showing interesting dielectric properties. Depending on the size of organic cation, its symmetry and ability to form hydrogen bonds a variety of polyanionic architectures can be realized which affect the dynamics of those crystals. Particularly attractive crystals appeared to be those containing small methylammonium, dimethylammonium and trimethylammonium cations. The hydrogen bonds formed between N-H groups and negatively charged halogen atoms are of medium strength so that some freedom of reorientations of those cations is possible.

In the present contribution we would like to review the results of recent dielectric studies on a number of crystals showing order - disorder phase transitions related to the dynamics of cations. In numerous crystals the transitions to ferroelectric, ferrielectric or ferroelastic phases were revealed. On the other hand in a case of the plastic-like crystals from this family one observes on cooling the freezing of almost free isotropic reorientations of alkylammonium cations. The discussion on the properties of these crystals is based on the studies of dielectric relaxation over broad frequency and temperature ranges as well as on structural, NMR and pyroelectric studies. Among various ferroelectric crystals grown in our laboratory a special attention evoked $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$ of high spontaneous polarization in polar phases and high peak of permittivity at 308 and 311 K, respectively. The mechanism of polarization in these crystals appeared to be fairly complicated because three non-equivalent methylammonium cations are present in the lattice at ambient temperatures.

RELATION BETWEEN STRUCTURE AND ELECTRICAL PROPERTIES OF h DIAMOND AND DIAMOND-LIKE STRUCTURES

G.W.Bąk[1], M Kryszewski[2], E.Staryga[1]

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During the last years a great interest in diamond and diamond-like carbon (DLC) structures is observed. This is both due to the preparation of synthetic diamond and application of comparatively cheap CVD technique for obtaining of DLC structures. The properties of DLC films will be the principal object of this paper. However, the comparison with diamond will also bc presented because diamond is a yard-stick material for all DLC and carbonaceous systems.

The structure of diamond and its relation to the physical properties are well known including also the diamond structures with various amount of C^{12} and C^{13} isotopes. Diamond is an indirect gap material with an energy gap equal to 5.49 eV. The drift mobilities of charge carriers (both electrons and holes) strongly depend on the concentration of impurities [1]

High-pressure high-temperature method of synthesis of diamond is rather expensive, thus since 1950 many works on synthesis of diamond and DLC structures by chemical vapour deposition (CVD) have been carried out. We will limit our discussion to the relation between the electrical properties of DLC and its structure considering mainly hydrogenated DLC (a-C:H) films because the knowledge of (a-C) films is less advanced.

The hydrogen content in DLC films depends both on the deposition technique and on the parameters of deposition [see e.g. 2, 3]. The physical properties of DLC films strongly depend on the relative amount of various chemical bonds which are created and which define many properties of these systems including their electrical characteristics. The DC conductivity and its activation energy can be correlated with the deposition conditions during CVD process [4] (see Fig.1). The temperature dependence of conductivity may be due to thermal excitations in a broad range of localised states. This conclusion is supported by the drift mobility measurements which also show the influence of the self bias during deposition of DLC films. The changes of the carrier transport conditions may be discussed in terms of various C-C and C-H bonds [5].

The influence of doping on the electrical propcrties of DLC films is rather difficult to be established because of the complex structure of DLC films themselves. Doping of the films obtained by r.f glow discharge with nitrogen, phosphine and diborane results in an increase in the conductivity by about 3 orders of magnitude and a decrease in both the width of optical gap and the activation energy [5]. Interesting results have been obtained by doping DLC structure with iodine. The films were obtained by the r.f. plasma method from methane with iodine as a source gas. The resistivity of iodine doped DLC films decreases by nearly 4 orders of magnitude as a result of doping. Contrary to the iodine doped DLC films deposited on n-type silicon, the iodine doped DLC films deposited on p-type silicon show a typical Ohmic behaviour [6]. This suggests that a:I-DLC is of p or p^+ type. The rectification ratio of undoped DLC/Si

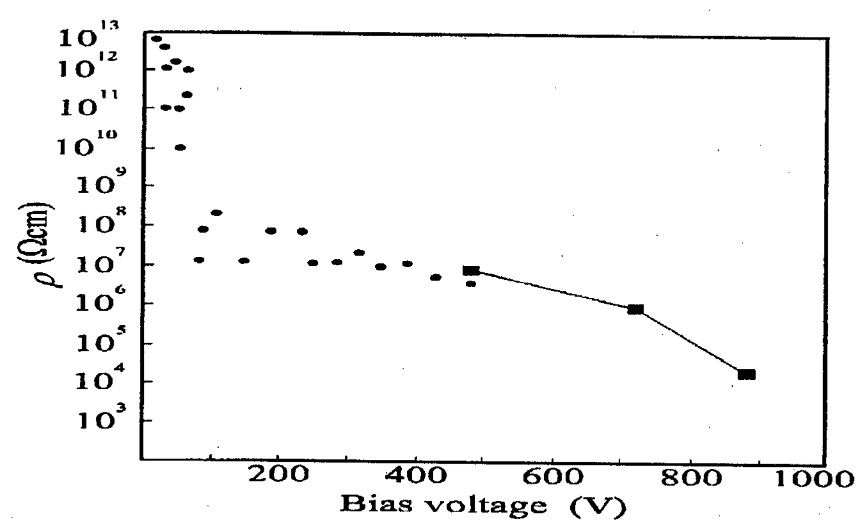

Fig.1. Resistivity as a function of the self bias voltage for DLC films obtained by RFPCVD technique. (•) Has et. al.[2]; (♦) Whang and Tae [7]. The substrate kept at room temperature.

heterojunctions does not exceed 10^3, but it can be improved by doping the DLC part of junction [8]. In this case the rectification ratio can reach 10^6. It may be concluded that doping may enable to obtain semiconducting DLC films of good quality.

There is no doubt that DLC films should be considered as an interesting material both for basic research and practical applications. However, despite a good deal of work carried out so far the relation between the deposition methods and the physical properties of DLC films needs further studies.

MK acknowledges the support of the KBN Grant 7-TOBE-066-14.p04 (Polish Committee for Scientific Research)

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MOLECULAR DYNAMICS OF POLY(ETHYLENE 2, 6 NAPHTHALATE) (PEN) BY DIELECTRIC SPECTROSCOPY

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The study is focused on the dielectric behaviour in relation to the evolution of the morphology of poly(ethylene 2,6 naphtalene dicarboxylate) (PEN). Such a work has been performed on amorphous and biaxially streched PEN films obtained from Du Pont de Nemours to evidence the relations between structure and molecular dynamics. This study was also carried out on these films after thermal treatments which can induced cold crystallisation for amorphous films or shrinkage and desorientation for biaxially oriented films.

The presence of naphtalene groups in the chain structure of PEN gives to the macromolecular chain a stronger rigidity and hence better physical properties than PET and explain the developpement of this polymer in capacitor,video tapes and packaging industries[1-3]. The understanding of the evolution of the morphology and orientation of PEN and the knowledge of their influence on physical properties is essential to forecast its properties for a given application.

A large panel of experiments have been performed to characterize the morphologies of these films. The percentage of crystallinity for the neat and the thermally treated samples and the cold crystallization temperature have been determined by Differential Scanning Calorimetry (DSC). FTIR spectroscopy using a wire grid polarizor has shown strong differences in crystallinity and orientation for selected vibrational bands. WAXS and SAXS allow to analyse the morphologies of the films in the α and β crystalline forms.

Relaxation phenomena have been studied using dielectric and dynamic viscoelastic analysis as this last one can give complementary informations about the origin of the different relaxations. The general appearance of the curves obtained by the two technics are similar. The so called α, β^* and β relaxtions[4] have been analyzed in terms of temperature shift and amplitude change according their evolution with the thermal treatments.

Dielectric spectroscopy has particularly been useful to compare the apparent activation energy, the VFT parameters and the dielectric increments for the different morphologies observed. In view to identify the local motions associated with secondary relaxations, some molecular mechanics calculations have been also performed.

The high temperature relaxation so called α relaxation has been associated to the glass transition and is assigned to chain segments cooperative motions which originate from conformational rearrangement of the main chains in the amorphous part of the polymer. This relaxation is modified by the confinement (fold, loops, tie chains) and restriction of amorphous chain configurations by crystals. In the semicrystalline oriented samples, the presence of tight coupling and extensive connections between the phases results in increased immobilization of this amorphous fraction. The two secondary relaxations β* and β are associated to movement out-of-plane of the naphtalene cycles for β* and to local movements of the chain including ester groups like in PET for the β one. The values of activation energies for these relaxations have been published elsewhere[4]. Some modifications of molecular motions can be sensitive to water uptake more or less according the type of relaxation : plastification effect for α transition and increase of the relaxation strenght for β relaxation.

We can also reported the possibility of using dielectric spectroscopy to analyze the cold crystallization by following the reorientationnal dynamics of dipoles in the frequency, time and temperature domain[8,9].

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FERROELECTRIC AND PYROELECTRIC POLYMERS,PROPERTIES AND APPLICATIONS

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UNIVERSITÉ PIERRE ET MARIE CURIE laboratoire des polyméres.
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Polymers exhibit many unique properties which open up numerous technological opportunities in the fields of optics and electrooptics. They combine the possibility of easy processing with an infinite potential for functionalization. They can thus be ferroelectrics, conductors or semiconductors, mesomorphous and can exhibit photoconductivity, piezo or pyroelectricity or nonlinear optical properties. These polymers give rise to a tremendous number of potential applications such as optical data recording, optical communications, displays.

This paper describes the properties and applications of some recent polymers in the field of ferroelectricity and pyroelectricity.

Ferroelectric poplymers appeared on the market around the eithies: at this time only the vinylidene difluoride (PVF2) existed.This polymer is semicrystalline and is obtained as a powder and then transformed in foil by extrusion and drawing.A dielectric permittivity around 10 can be interesting for the capacitors.The ferroelectric phase witch exhibits piezoelectricity and pyroelectricity is, however, not the natural crystaline phase that is to say that the PVF2 film has to be streched in order to obtain the beta non centrosymetric phase.

The vinylidene difluoride and trifluoride copolymers appeared more recently and are very interesting due to their processability.

Other polymers, such as side-chain polymers exhibit liquid crystaline phases such as chiral smectic C phase.and are also ferro or pyroelectric.

we will describe the different properties of these polymers.

An other part of this talk concern the applications of these polymers in IR detection. IR detection in the 8 - 14 μm band is realized today essentially by semiconductors working at 77_K which needs expensive and bulky cooling systems The realization of sensors working at room temperature using integrated silicon circuit manufacturing technology opens up the possibility of manufacturing IR sensors with characteristics similar to the sensors working in the visible range1.Different companies, such as Thomson-CSF,have carried out researches in the field of IR sensors working at room temperature using ferroelectric and pyroelectric copolymers of poly (vinylidene fluoride) and trifluoroethylene.This copolymers are soluble and easy to process by the standard technique of CCD silicon circuit.

We will describes some realisation of matrix array detector associating the P(VF2-VF3) copolymer with silicon CCD matrix.

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THE DIELECTRIC RELAXATION IN COMPLEX SYSTEMS

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The presented contribution is centered around the area of condensed matter physics for investigation of the structure, dynamics, and macroscopic behavior of materials which can be characterized as *complex systems (CS)*. "Complex" here refers to the fact that the systems possess at least one degree of freedom beyond the usual translation one in "simple" fluids and/or non-crystalline solids. CS are a very broad and general class of materials which include associated liquids, polymers, biomolecules, colloids, etc.)

CS involve the appearance of a new ("*mesoscopic*") length scale, intermediate between molecular and macroscopic. Fast as well as ultra-slow molecular rearrangements take place in the presence of the microscopic, mesoscopic and macroscopic organization of the systems. The complete characterization of these relaxation behaviors requires the use of a variety techniques in order to span the relevant ranges in frequency. To obtain this information, noninvasive methods such as Dielectric Spectroscopy (DS) is very advantageous. The unique technique with wide frequency (10^{-3}–10^{11} Hz) and temperature (–170°C ÷ +300°C) ranges of that method is more then any others appropriate for such different scales of molecular motions.

The dielectric relaxation behavior in porous glasses for example can provide the information on the geometry of pore size distributions, fractal dimensions of the porous matrixes and the mesostructural features of water which can easily be absorbed on silica layers. The obtained information about the cooperative relaxation processes of water molecules absorbed in the confined volumes allowed us to understand the molecule structure and properties of water absorbed on the pores surface and determine the morphology and structural transitions in the porous systems.

The complex dielectric behavior of the studied porous glasses versus frequency and temperature can be described in terms of the four distributed relaxation processes. For a quantitative analysis of the dielectric spectra for the first, second and third processes a formula of superposition of Havriliak-Negami (HN) and Jonscher's empirical term $(i\omega)^{(n-1)}$ has been fitted to the isothermal dielectric loss data. In the case of the fourth process the superposition of the HN function and a conductivity contribution was used.

The study of the porous glasses leads to several new features in their dielectric behavior: (i) The dielectric relaxation of porous glasses is very sensitive to the cooperative dynamic of water molecules filling the pores and geometrical micro- and mesostructural features of the porous matrix; (ii) The dielectric relaxation behavior of different porous glasses is associated with the complex dynamics of water molecules and reflects their interactions with the pores surface; (iii) Analysis of the dielectric spectra of the porous glasses enables us to calculate the fractal dimension and porosity of the materials.

HIGH SPACE-CHARGE DENSITIES IN NON-POLAR AND POLAR DIELECTRICS

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Uniform or non-uniform space-charge densities of up to $1\,\mathrm{kC/m^3}$ corresponding to trapped-charge number densities of up to $10^{16}/\mathrm{cm}^3$ can be achieved in several nonpolar fluoropolymers that are based on polytetrafluoroethylene by means of high-field charging for extended time periods at high temperatures. Under suitable conditions, the charging of the sample volume works equally well for both polarities. The resulting charge-density profiles across the sample thickness are probed with piezoelectrically generated acoustic step waves in order to control the charging process with respect to the overall charge density and its spatial distribution.

High charge densities are also found at the crystallineamorphous phase boundaries in polar ferroelectric fluoropolymers based on polyvinylidene-fluoride where they seem to be necessary for electrically compensating and thus stabilizing the dipole polarization of the crystallites. Sophisticated poling schemes in which the fields and the temperatures are appropriately chosen above and below the coercive field and the glass-transition temperature, respectively, allow for selective polarization of the two phases or the interface between them.

Since the two families of fluoropolymers are chemically relatively similar, it may be speculated that the rather stable charge trapping in both groups may have similar microscopic origins. Ongoing work on the production of high space-charge densities and on the clarification of charge-trapping mechanisms in non-polar and polar fluoropolymers will be reported and discussed.

EPITEXIAL COMPLEX–OXIDE HETEROSTRUCTURES : PROCESSING, CHARACTERISATION AND APPLICATIONS

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Abstract not available

STRUCTURE RELAXATION IN SOME PROTONIC CONDUCTORS

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Some hydrogen sulphates and selenates of monovalent cations were found to exhibit a transition to phase characterized by fast structure diffusion of protons at well defined temperature T_s [1–5]. Fast proton transport at $T > T_s$ resides in almost barrierless proton transfer between neighbouring $X0_4$ tetrahedra and subsequent reaorganization of proton environment (Grotthuss mechanism) [6-8]. The superprotonic phase is characterized by high structural disorder :
i) translational disorder of protons in hydrogen bonds
ii) orientational disorder of $X0_4$ groups (vibrational and librational modes) and iii) orientational disorder of NH_4 groups in ammonium containing crystals.

Tetraammonium dihydrogen triselenate undergoes a transitian to superprotonic phase at $T_s = 378$ K and the phase is characterized by isotropic proton transport with activation energy of 0.11 eV [4]. When the crystal is cooled down from the highly disordered superprotonic phase to the low conducting one the well defined protonic order, characteristic of the low temperature lattice structure, has to be recovered. The relaxation of the structure is a complex process and is characterized by complicated energy landscape. The relaxation of the structure of $(NH_4)_4H_2(SeO4)_3$ single crystals was studied by means of NIR Raman spectroscopy and impedance spectroscopy.

At room temperature, in the low conducting phase, the $(NH_4)_4H_2(SeO_4)_3$ crystal is triclinic (space group $P\bar{1}$) [4, 9] and consists of trimers formed by three SeO_4 tetrahedra linked with hydrogen bonds and lying along $[0\bar{2}1]$ direction [10]. The $Se(2)O_4^{-2}$ ion is located in the center of the trimer and its two O(22) and 0(23) oxygens play a role of proton acceptors in the two hydrogen bonds with the two outlying $HSe(1)O_4^{-1}$ and $HSe(3)O_4^{-1}$ anions.

As the dynamics of SeO_4 tetrahedra determines the proton dynamics we were interested in the behaviour of SeO_4 skeletal modes. Time variation of NIR FT Raman spectra after cooling the crystal from the superionic phase to various $T < T_s$ was studied using Bruker FRA106 Raman spectrometer. The SeO_4^{-1} and SeO_4^{-2} stretching modes, characteristic of the high temperature phase [11], were observed in the low conducting phase for a dozen of mins and after this time the bands, characteristic of the low conducting phase were recovered contineously. We observed, however, in the Raman spectrum of the crystal cooled from the superionic phase a band at ~735 cm^{-1}, which does not exist neither in the high nor in the low conducting phase. The band exhibits characteristic kinetics and disappeares but at the same time the $HSeO_4^{-1}$ band (at 725 cm^{-1}) starts to rise. The behaviour of the mode at ~735 cm^{-1} we relate to a formation and disapperance of O_3SeO–H...$OSeO_3$ dimers as a transitional form before the trimer formation.

Impedance spectroscopic studies of the time variation of protonic conductivity after cooling the crystal from the superionic phase to low conducting phase revealed also three rates of the conductivity decrease to the stationary value, characteristic of the virgin sample.

The results obtained can be sumarized as follows: when $(NH_4)_4H_2(SeO_4)_3$ crystal is cooled from highly disordered superprotonic phase to low conducting phase the protonic order, characteristic of the low temperature phase (ordered trimers) has to be recovered. Time changes in SeO_4 skeletal modes points to the following processes of the recovery:

i) relaxation to the low temperature molecular structure - formation of the trimers, characteristic of the low conducting phase is preceeded by formation and disappearance of dimers ;

ii) relaxation to the low temperature crystallographic structure - the process is complex and apparent in conductivity and DSC studies [12].

We observed that the process of the dimer formation and disapperance proceeds within ~30 mins at T = 303 K, whereas the formation of the trimers lasts ~1 h at the same temperature. It was observed, moreover, that about 6 weeks is needed to establish the long range crystallographic order in the crystal at room temperature.

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PHYSICS OF LOW-LOSS DIELECTRICS

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Low-loss dielectrics present a number of very interesting questions which challenge our concepts regarding the dielectric response. Among these may be mentioned:
1. the generally observed "flatness" of the frequency dependence of the loss and its theoretical significance;
2. the breakdown of the "universal" relationship found in most other materials and the consequences for the theory;
3. the problem of how low losses can be obtained in the presence of significant amounts of dipolar and other impurities which are inevitably present in most practical dielectrics.

The first property implies that energy loss per reversal of polarisation isindependent of frequency in wide limits and this calls for specific physical mechanisms, of which piezo-electric processes may be typical. The breakdown of the universal relationship suggests that there must exist other relationships which give a different frequency dependence and a different relationship between the real and imaginary components of the permittivity. Some examples of such relationships will be discussed. The third question is of considerable practical significance and the suggested answer lies in the screening effect of dipoles which will be discussed.

HIGHLY ORIENTABLE SIDE CHAINLIQUID CRYSTALLINE POLYMERS FOR QUADRATIC NONLINEAR OPTICS

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There exists a large class of practical applications which require a use of noncentrosymmetric materials. These applications include: frequency doubling, electro-optic modulation, frequency conversion and photorefractive effect. Composite polymeric, materials have emerged to be interesting materials for these kind of applications. They are inexpensive and can be easily processed into good optical quality thin films. The active chromophore orientation is obtained by static field[1] or all optical poling[2]. However, the quantity of interest, which is the macroscopic second order nonlinear optical susceptibility, depends on the polar order through the following, well known relation:

$$\chi^{(2)}(-\omega_3;\omega_1,\omega_2) = NF < \beta(-\omega_3;\omega_1,\omega_2) > \qquad (1)$$

where N is number density of NLO active molecules, F is the local field correction and β is the molecular first hyperpolarizability, and the brackets denote its orientational average. Optimization of the macroscopic susceptibility $\chi^{(2)}$ is possible not only by inreasing the β value through molecular engineering or number density N but also by an increase of orientational order. Liquid crystals (LC's) are of particular interest in this sense because their properties of self organization give rise to system with high axial order, which can be used to enhance the polar order, intervening in Eq. (1). Such an enhancement has been predicted by a number of molecular statistical models. Especially interesting the are side chain LC polymers which offer the possibility of processing. Gonin et al[3] have recently demonstrated experimentally that LC's polymers exhibit a gain in polar ordering by a factor of 2.3-3.3 over the isotropic counterparts.

In this paper we review the results of our systematic studies of second order nonlinear optical properties of side chain liquid crystalline polymers functionalized with cyanobiphenyl chromophore. Several polymer backbones have been used, leading to polymers with different glass transition temperatures. The kinetics of the growth of axial order has been studied by the measurements of the variation of optical absorption spectrum by applying external DC field using the corona discharge technique. The growth of polar order as well as its relaxation was studied by the *in situ* second harmonic generation technique. These studies show importance of initial polar order for the corona poling efficiency favoring in this way liquid crystal materials. The efficiencies of polar and axial orderings are compared with theoretical predictions within different orientation models.

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MOLECULAR DYNAMICS IN SMALL CONFINING GEOMETRIES: FROM THE SINGLE MOLECULE TO THE LIQUID STATE

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Broadband dielectric spectroscopy (10^{-2}Hz - 10^{9}Hz) is employed to study the molecular dynamics of (glassforming) guest molecules being confined to xeolithes and nanoporous glasses. Depending on size and topology of the host ambience for the same guest molecule (ethylenglycol) the transition is observed from a single-molecule relaxation to a liquid-like dynamics. - The dynamic glass transition of van der Waals and of H-bond forming liquids takes place in a nanoporous environment (pore size: 2.5 nm, 5.0 nm and 7.5 nm) on a time scale which is comparable to the bulk. Due to surface effects a broadening of the relaxation time distribution and a slight decrease of the mean relaxation rate (2.5 nm pores) is observed for H-bonded systems. This effect can be counterbalanced by lubricating the inner surfaces of the pores. By that the molecular dynamics of the molecules inside the pores is decoupled from the solid walls. For the van der Waals liquid salol in lubricated pores the mean relaxation rate becomes by up to two decades faster than in the bulk. This paradox confinement effect is the more pronounced the smaller the pores are. It reflects the inherent lengthscale of cooperativity of the dynamic glass transition.

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SPACE CHARGE CHARACTERIZATION FOR INSULATOR SPECIFICATION. *NEW SPECIFICATIONS FOR PRODUCTIVITY AND QUALITY IMPROVEMENT.*

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Insulator standard specifications are not enough to help the material user who wants to predict how his material will behave under his own operational stresses (temperature, electric field, mechanical stress, environment). This statement will be illustrated in order to demonstrate that specifications reflect the material manufacturer and user technological experiences of but are not based on fundamentals that explain aging, breakdown, fracture, adherence loss, etc. Standard specifications are "global" measurements achieved under stresses that are very different to the operational stresses. In the XXI th century the goal will be to improve specifications for obtaining a maximum number of information with doing the minimum number of tests. It is believed that such possibilities are offered from the characterization of charge and energy localization phenomena in insulators. The key point is that charge trapping involves both characteristic sites and the electro-mechanical characteristics of the site surrounding matrix. The site-environment coupling is reflected by the material internal energy variation as function of the polarization and by energetic exchanges during charge relaxation. Another key point is that the lattice relaxation occuring after the charge relaxation is an exothemic reaction. Whatever the relaxation mechanism (phase transition, electrochemical reaction) the balance between the energy released rate and the energy loss determines whether or not the catastroph may propagate. This approach applies to fracture and beakdown and revisits the physical meaning of the Griffith's theorem terms. Charges can be injected under electric field or under electrostatic chargers. It is noteworthy that sample preparation, charge injection and charge measurement techniques have to be non destructive for preserving the material intrinsic defects. Also, charge injection conditions (field, temperature, dose, dose rate) cannot be arbitrarily chosen but have to be determined in order to reflect the material charge trapping-detrapping characteristics. Moreover, charge injection has to be achieved in order to avoid the convolution of all the elementary phenomena that deal with the story of injected charges in the insulator and to avoid the convolution with instrumental effects. When these conditions are not fulfilled the measurement is often limited to an average charge distribution measurement. New specifications include the trapping characteristics, these characteristic variations as function of stresses and the charge detrapping characteristics. An electron beam technique has been developped for such measurements and applied to Etectrotechnics and Mechanics. Examples will be shown.

A MODEL OF LONG TIME DECAY OF SPACE CHARGE IN POLYMERS

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The real or polarizing charge present in dielectric sample produce not only external but, in most cases, also a strong internal electric field $E(x)$. Assuming the unidimensional case with axis x perpendicular to the surface of dielectric plate the intensity of field $E(x)$ is expressed by[1]

$$E(x)=\frac{1}{\varepsilon_0\varepsilon}\left(\int_0^x \rho(x')dx' - \hat{\sigma}_1 - \frac{\hat{\sigma}_2}{1+x_D/(\varepsilon x_g)}\right)$$

where ε_0 and ε denote the electrical permittivity of vacuum and relative permittivity of the dielectric, respectively. x_D and x_g are the respective thickness of dielectric and air gap, while $\rho(x)$ denotes the sum of real free (space) charge and imaginary polarizing charge density. $\hat{\sigma}_1$ and $\hat{\sigma}_2$ denote the first moment of charge distribution or the *effective* densities of charge on both surfaces of electret.

However, the electrical conductivity of all materials has a finite value. *The current carriers are moving in field E(x) as long as a full compensation of charge has been achieved within the entire volume of the electret.* The electrical conductivity G of Teflon® film, which is one of the best known insulators, measured under normal conditions is of the order of 10^{-19} S/m or higher, depending on purity and sample thickness[2], which corresponds to electret life-time of few month only. Why then the observed electret life-times are several order of magnitude longer[3] ? The mechanism of electrical conduction in dielectrics should explain this divergence.

A model assuming *a competition between the rate of current carriers creation β in activation processes, and the rate of carriers annihilation on electrodes and by free, implanted charge* was considered. The two cases was analysed: an uncharged dielectric in external DC field, and a dielectric in internal, time-dependent electric field produced by an implanted charge.

For the first case for very small rate β, e.g. for large energy gap and deep traps, the current density j, after the time t much longer than the flow-time ($t \gg x_D/(Eu)$), no longer depends on the strength of the electric field[4], and is equal to $j=GE=\beta q x_D$, where q denotes the charge of current carriers. In consequence, final conductivity the is proportional to the thickness of dielectric plate in excellent agreement with results obtained by the main Teflon® producer, Du Pont[2].

For the second case we assumed that there was no external current source, and metallic electrodes are shortened and grounded. We also assumed that the internal electric field is uniform and can be expressed by approximate equation $E \cong \hat{\sigma}_D/(\varepsilon_0\varepsilon)$. Denoting the initial (undisturbed) values of conductivity and current carriers density as G_0 and n_0, respectively, the time evolution of electrical conductivity $G(t)$ and density of implanted charge $\hat{\sigma}(t)$ due to the current carriers moving in the field generated by the charge can be described for unidimensional case by the following set of the two differential equations:

$$\frac{d\,G(t)}{dt} = \frac{\beta}{n_0}\left(G_0 - G(t)\right) - \frac{u}{\varepsilon_0 \varepsilon x_D} G(t)\,\hat{\sigma}(t)$$

$$\frac{d\,\hat{\sigma}(t)}{dt} = -\frac{G(t)\,\hat{\sigma}(t)}{\varepsilon_0 \varepsilon}$$

The discussed processes lead to a very pronounce decrease in electric conductivity, and in consequence to long life-times of implanted charge, in agreement with experimental data. For parameters specific to the low-conducting polymers like polyethylene or Teflon®, the electrical conductivity $G(E,t)$ decreases exponentially over several orders of magnitude with the decay time of the order of several days (Fig. a). Afterwards, in long time scale, conductivity very slowly recovers eventually reaching its initial value after thousands of years (Fig. b).

Parallel to this effect, the density of implanted charge $\hat{\sigma}(t)$ is partially com-

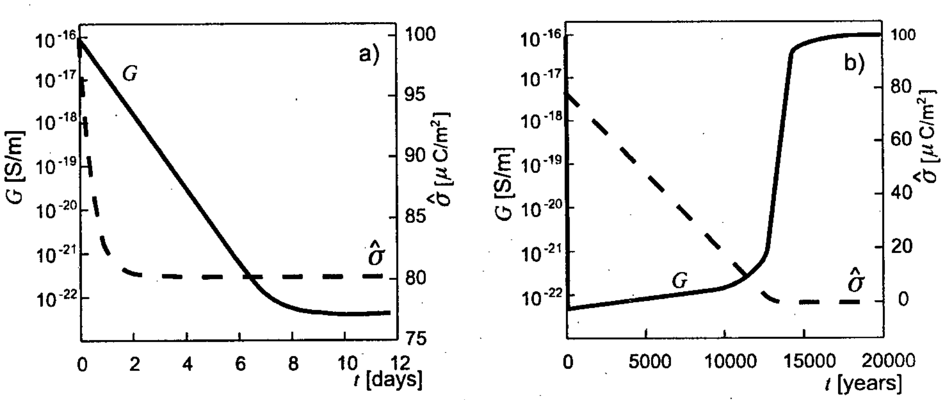

Fig. 1. Electrical conductivity G and charge density $\hat{\sigma}$ *versus* linear time scale t for short times (a) and long times (b). u=10^{-16} $m^2\,V^{-1}\,s^{-1}$; ε=2; x_D=20 μm.; β=$6\times10^7\,s^{-1}\,m^{-3}$.

pensated during the first hours or days. This is the first step of charge decay with the relaxation time close to the flow-time of carriers (Fig. a). The fraction of charge which survives the first step strongly depends on the initial charge density. The second step of charge decay is very slow and linear. The slope of the decay is proportional to the rate of carriers creation and thickness of dielectric plate. The evaluated typical times of the decay are of the order of 10^2-10^4 years, in accordance with the experimentally observed life-times of electrets (Fig. b).

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CORRELATIONS IN SYSTEMS WITH COMPLEX DYNAMICS

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Problems concerning complex dynamics will be discussed for case of isopentyl cyanobiphenyl sample with chiral dipolar molecules. First the results of DSC, polarizing microscopy and far infrared will be presented in order to show the phase diagram which is the following [1].

Glass $\Leftrightarrow$ Cholesteric phase $\Leftrightarrow$ Supercooled isotropic liquid $\Rightarrow$ Crystal $\Rightarrow$ Isotropic phase.

Further, the dielectric relaxation investigations at the frequency range from 10^{-1} to 10^{5} Hz will be shown [2]. Relaxation observed is a single process in the isotropic phase and a bimodal process in the cholesteric phase. This complex relaxation has been separated into two processes of ColeDavidson type. The stronger one extracted at lower frequencies fulfills well the Vogel-Fulcher dependence with T_0 = 172 K. This α-process ascribed to reorientations of molecules around the short axes slows rapidly with lowering the temperature and points to the ftagility of about 40 [3]. The Jonscher correlation parameters are independent of temperature and equal m = 1 and n = 0.5. The extracted data of ε' and ε'' have been used to present the analyzed process in the form proposed by Dixon and co-workers [4]. The universal curve covers 12 decades of frequency. The scaling proposed by Abe and co-workers [5] has given for our data the worse agreement at higher frequencies. The crystallization process of the supercooled isotropic phase observed for this sample on heating we described in terms of Avrami equation [6].

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MICROWAVE HEATING AND THE ACCELERATION OF POLYMERIZATION PROCESSES

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Among the nearly innumerable industrial, scientific, domestic and medical applications of microwave power heating of dielectric substances, those in physical or chemical processing of polymeric materials play an important role from over a quarter of a century.[1] In the last field, the rubber industry is known to make the most extensive use of this heating technology since the early 1970s, in particular to boost the uniform heating of extrudates, and thus promote their fast, continuous vulcanization (often suitably associated with chemical foaming).

Besides this, microwave energy is also being employed in industry in a great variety of cases, or has been experienced by many investigators, as a means of causing the extremely rapid and/or selective heating of thermoplastic polymers and thermosetting resins.[1] This in order to accomplish their quick drying (in case their are applied as solutions or aqueous dispersions), and their very fast to almost instantaneous melting or chemical hardening, respectively.

Similarly to what done in the rubber industry, however, microwave heating has long time been considered and utilized as a *physical* way to perform rapid, thermal transformations of materials or chemical processes. It was only in the 1980s, in fact, that microwave irradiation revealed the capacity of inducing remarkable-to-strong reaction accelerations (and even modifications of pathway and/or final yield) in an impressive variety of chemical processes, including step- and chain-growth, di- and multifunctional polymerizations,[1,2] as well as numerous organic syntheses.[3] Many years in advance, activation phenomena in biological tissues were highlighted in medical microwave diathermy. Such effects on chemical and biochemical processes, claimed by most investigators to be independent of the microwave heating regime, and analogous to catalytic influences, are now jointly referred to as *nonthermal* or *specific* effects of microwaves.

Whereas outstanding reaction accelerations under microwave heating are nowadays well recognized and exploited in analytical chemistry,[4] the interpretations and even the reality itself of them in both polymer and organic chemistry are still controversial.[5] Chemical justifications are hard to give, indeed, for such effects of microwave radiation, whose quantum energy always is even lower than the dissociation energy of the weakest (noncovalent) molecular interactions. Physical explanations proposed, most of which implying dynamic, non-equilibrium distributions of temperature, include: (i) selective overheating of dipolar reacting groupings; (ii) statistical generation of rapidly transient hot spots (conceptually similar to the mechanism of sonochemical processes in liquids, *via* acoustic cavitation); (iii) simple, local superheating at macroscopic level; (iv) accelerated hopping transport of ionic reacting species, and others.[5]

The most extensively studied class of polymerization processes under microwave heating is the accelerated curing of thermosetting resins: unsaturated polyesters, epoxy/amine and epoxy/isocyanate systems, bismaleimides and bisnadimides, etc.[1,2,5] In recent years, a variety of (cyanoalkoxyalkyl) trialkylammonium halides have been appropriately synthesized as strongly microwave-absorbing, hardening catalysts for slow-curing epoxy/aromatic isocyanate[6a] and aliphatic or cycloaliphatic epoxy/anhydride[6b] thermosetting systems. Tables 1 and 2 show the gelation and vitrification times measured in the isothermal cure of the two systems: (a) liquid bis(isocyanatophenyl)methane (MDI) + diglycidylether of bisphenol A (DGEBA), with [3-(2-cyanoethoxy) propyl] (dimethyl) decylammonium iodide (1.90 mmol/100 g) as the catalyst; (b) 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanoate (ERL-4221™ , Union Car bide) + hexahydrophthalic anhydride (HHPA), catalyzed by 4-[2-(cyanoiso propoxy)ethyl] (4-pentyl) morpholinium iodide (CN4). These data exemplify the remarkable curing accelerations attainable under microwave versus conventional heating, with such specific catalysts. For the epoxy/anhydride system (b), reaction rate gains over a conventional catalyst, even though used in a higher molar concentration (tetrabutylammonium iodide (TBAI)) are also exemplified.

Table 1 MDI/DGEBA 70:30 w/w system; isothermal cure at 66°C

Heating type	*Gelation time*	*Vitrification time*
Conventional heating	~ 40 min	> 180 min
Microwave heating	?	15 - 20 min

Table 2 ERL-4221/HHPA system; isothermal cure at 85°C			
Heating type	*Catalyst*	*Gelation time*	*Vitrification time*
Conventional	CN4 (1.14 mmol/100 g)	~ 270 min	> 450 min
Microwave	CN4 (1.14 mmol/100 g)	?	60 min
Microwave	TBAI (1.52 mmol/100 g)	~ 120 min	?

More recently, computational approaches have been applied to potential molecular mechanisms of microwave effects in both chemical systems. Their polymerization is recognized to proceed *via* intermediate anionic species, resulting from opening of epoxide or anhydride rings attacked by the catalyst's halide ions. By the semi-empirical quantum mechanics methods AM1 and PM3,[7] exceptionally-high dipole moment values *in vacuo* (i.e., in excess of 12 Debyes) have been calculated for many (2-cyanoalkoxyalkyl) trialkyl-ammonium cations. According to molecular models *in vacuo*, these countercations should act as localized, molecular *microwave overheaters* of reactive anion centers in the vicinity of which they are, and whose apparent reactivity might thus be correspondingly enhanced. Investigations are still in progress *via* molecular dynamics simulations of heating and cooling processes.

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DISPERSIVE RATE PROCESSES IN CONDENSED MEDIA

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Rate processes for which many time scales coexist are called dispersive, cf. Scher et al.[1] presentation of the dispersive transport and relaxation, and the author's account[2] of the development of dispersive chemical kinetics. Dispersive rate processes are endemic in condensed media[3-6].

The rate coefficient for dispersive processes do depend on time. In the case of chemical reactions, the time dependence of the rate coefficients, $k(t)$, called *specific reaction rates*, was rationalized in the following way[2]. Reactions by their very nature have to disturb reactivity distributions of the reactants in condensed media as the more reactive species are the first ones to disappear from the system. The extent of disturbance depends on the ratio of the rates of reactions to the rate of internal rearrangements (mixing) in the system restoring the initial distribution in reactivity of reactants. If the rates of chemical reactions exceed the rates of internal rearrangements, then the initial distributions in reactant reactivity are not preserved during the course of reactions and the specific reaction rates depend on time. If, however, the rates of internal rearrangements exceed markedly the rates of chemical reactions, then the extent of disturbance is negligible and classical kinetics, with constant specific reaction rate, k, called *reaction rate constant*, may be valid as an approximation. Thus in the limit of efficient renewing of reactant environment the classical kinetic patterns with constant specific reaction rate are recovered; the reaction system appears to be homogeneous. It is easy to extend the above reaction picture to include other dispersive rate processes in condensed media and to find similar effect of system internal rearrangement on the coefficients for dispersive transport and relaxation. It is also possible to extend the traditional interpretation of the constant specific reaction rate in terms of energy profile along the reaction path to time-dependent specific reaction rate and time-dependent activation energy. New perspectives are, however, seen[6] as the once abstract notions of fractal space and time, used in stochastic models of dispersive kinetics, now appear naturally and inevitable in chaotic dynamics[7].

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ON THE HIGHER MOMENTS OF DIELECTRIC POLARIZATION

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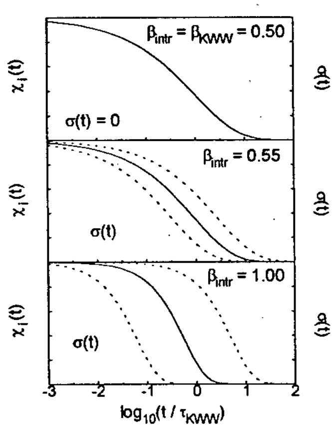
The normalized time dependent reponse of dielectric relaxation processes is usually a non-exponential monotonic decay, which is often well characterized by the Kohlrausch-Williams-Watts (KWW) or stretched exponential of the form

$$\Phi(t) = \exp\left[-(t/\tau)^{\beta}\right] .$$

Alternatively, $\Phi(t)$ can be written as a superposition of exponentials, where an appropriate choice of the probability density $g(\tau)$ can again lead to a KWW type form of $\Phi(t)$. We generalize this latter approach by assuming a superposition of KWW type basic functions, combined with a $g(\tau)$ which leads to an overall stretched exponential function for $\Phi(t)$ [1]:

$$\Phi(t) = \exp\left[-(t_{KWW}/\tau)^{\beta_{KWW}}\right] = \int_0^{\infty} g(\tau)\exp\left[-(t/\tau)^{\beta_{intr}}\right] d\tau .$$



This form models the situation of non-exponential elementary processes combined with a possible (spatial) distribution of relaxation times. An experimentally given data set for $\Phi(t)$ can now be fit equally well by an infinite set of β_{intr} ($\geq \beta_{KWW}$) values. The case $\beta_{intr} = \beta_{KWW}$ results in $g(\tau) = \delta(\tau - \tau_{KWW})$ and refers to dynamical homogeneity, while $\beta_{intr} = 1$ signals the extreme heterogeneous limit, in which the non-exponentiality of $\Phi(t)$ originates solely from the relaxation time τ being a spatially varying quantity. Macroscopic techniques, like standard dielectric relaxation experiments in the linear response regime, remain incapable of discriminating between heterogeneous and homogeneous dynamics.

We use optical techniques in order to measure the highly local effects of dielectric polarization in the electric fields of probe molecules. This method of solvation dynamics experiments yields not only the average value of the time dependent polarization, but also higher moments thereof, e.g. the variance [2]. From such data we are able to derive the variance of the elementary decays $\exp[-(t/\tau)^{\beta_{intr}}]$ with respect to the probability density $g(\tau)$, which translates into an experimentally determined value of β_{intr}. From the result $\beta_{intr} \approx 1$ we conclude that a spatial distribution of relaxation times is responsible for the overall stretched exponential form of dielectric polarization. This result is at variance with the serial relaxation scheme proposed by Palmer et al. [3] in order to rationalize KWW type correlation functions.

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THEORETICAL TREATMENT OF PHASE TRANSITION ANOMALIES IN DIELECTRIC WITH STATIC RANDOM DISORDER

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Abstract not available

SCANNING PROBE MICROSCOPIES IN THE STUDY OF DIELECTRICS

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Historically, we have been largely preoccupied with obtaining a macroscopic view of the behaviour of dielectric materials using assessment techniques and mathematical models that operate on length scales resolvable by the naked eye. This has served engineering developments well despite the lack of a more detailed scientific understanding of microscopic phenomena and processes. Scientific interest has been shown in microscopic and sub-microscopic behaviour of physical processes but observation has been constrained by the absence of suitable experimental techniques.

In the last decade this position has progressively changed, driven by the need to understand localised characteristics and processes. In turn this has led to the development and application of a number of surface microscopies and spectroscopies capable of providing qualitative and more recently quantitative information on a variety of physical and chemical characteristics at mesoscopic and nanoscopic length scales.

This paper deals with a number of these developments with special emphasis on so called scanning probe microscopy (SPM) methods with spatial resolutions ranging from microns to nanometres both in the plane of the surface and normal to the plane[1]. In particular we will consider atomic force microscopy in providing nanoscopic topographic information and its comparison with laser scanning confocal microscopy. We extend this by considering electrostatic force microscopy and its variants. These can in principle provide microscopic spatial information on permittivity variance, surface potential and the static and dynamic behaviour of surface and subsurface charge [2].

Atomic Force Microscopy

Following the development of atomic force microscopy (AFM) in 1986, commercial instrument development has enabled the technique to be widely applied, with continual improvements in spatial resolution and an increase in the number of contact and recently non-contact modes of operation. Sub-nanometre resolution in the x-y plane in contact mode is possible with molecular resolution achievable with suitable substrates and probes.

The key advantage of AFM is it's ability to produce quantitative z-direction information, a capability it shares with laser scanning confocal microscopy (LSCM), albeit that the latter achieves this by overlay of z-incremented images in contrast to a single-scan in AFM. LSCM also has a resolution of around 0.2 microns in comparison with nanometre/molecular resolution in AFM. Comparisons of electron, optical and scanning probe microscopies will be presented to illustrate the additional insight provided by AFM. Results will be presented from surface modified polymers resulting from exposure to activated species from atmospheric pressure plasmas.

ILLUSTRATE THE POTENTIAL OF THE TECHNIQUE IN THE STUDY OF MICROSCOPIC CHARGE DISTRIBUTIONS IN DIELECTRICS. WE WILL ALSO DESCRIBE RECENT WORK ON MODELLING THE PROBE-SAMPLE INTERACTION.

WE WILL SHOW BY REFERENCE TO THE LITERATURE AND OUR OWN WORK ON EFM

Should be added to the book of abstracts, page 34

presented to illustrate the additional insight provided by AFM. Results will be presented from surface modified polymers resulting from exposure to activated species from atmospheric pressure plasmas.

Electrostatic Force Microscopy

EFM was developed 2 years after AFM but until very recently it has been the domain of those with specialist microscopes. Unfortunately, the technique has not experienced the same rate of development as AFM and detailed understanding of the mechanisms of image formation have not been obtained. Consolidation work is in progress[2] and we will illustrate the potential of the technique in the study of microscopic charge distributions in dielectrics. We will also describe recent work on modelling the probe-sample interaction.

We will show by reference to the literature and our own work on EFM[2] that it is possible to measure the spatial distribution of localised surface and subsurface charge with spatial resolutions approaching 200nm or better and charge resolutions of 5-10 electrons or less. We will also provide examples where both positive and negative charge can co-exist in close proximity on dielectric surfaces such that conventional macroscopic charge probe methods would either not detect the charge or would reveal the presence of only a small level of net excess charge.

Within the constraints of current sampling timescales in EFM (e.g. line scans typically 2 - 10 seconds) it is possible to study the dynamics of surface charge including charge deposition/injection and dissipation spatially. These capabilities will be illustrated by reference to results from current work in progress at Surrey and in the literature.

Future Developments

Scanning probe microscopies are continuing to develop rapidly with both topographic, chemical and physical measurement capability. The concept of a laboratory on a tip is progressively being realised. In the next 5 to 10 years it is likely that we will be able to quantitatively measure many surface and bulk characteristics including dielectric, optical, electronic, electrical, mechanical (including adhesion and binding) and thermal properties with mesoscale and nanoscale resolutions in the x, y and z directions.

Chemical information will also be available from probe spectroscopies facilitated by the development of scanning near field optical methods and others appraoches such that most of the current optical, vibrational and molecular spectroscopies and spectrometries will be possible with sub-micron spatial resolutions. These developments will further contribute to our understanding the surface and bulk characteristics of dielectrics and at a more fundamental level allow us potentially to manipulate these characteristics at a nanoscopic and molecular level.

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DIPOLAR SPECIES IN MOLECULAR MATERIALS AS CHARGE CARRIER TRAPS

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The role of localization of charge carriers in determining electrical properties of molecular materials has been recognized quite early [1-3]. One of the questions which should be addressed in this context is the one concerning the nature of local centres. A model has been put forward [4,5] based on the electrostatic model of Lyons [6,7], explaining the appearancc of traps for charge carriers. It was pointed out [4,5,8,9] that molecules localize charge carriers if their molecular ionization energy is smaller and/or their electron affmity greater than the respective values of the host molecules (i.e., if they are chemically different fi-om the host ones), or if the absolute value of the polarization energy is locally greater than that in a perfect crystal (i.e., if a carrier encounters a physical defect of the crystal structure). The polarization energy ($P<0$) is the energy of interactions between a charge localized on a given site and the surrounding polarizable medium; in many non-polar crystals its value ranges between -1.5eV and -2.5eV [2,3,6,7].

Of interest is the situation when a molecular system consisting of non-polar or weakly polar species is doped with polar guest molecules. One may envisage the following effects:

(*i*) If the electron affinities and/or ionization energies of the host and guest molecules fulfil at least one condition mentioned above, then the guest molecule itself may act as a chemical trap. In this case the detrapping of charge carriers from such traps may be field-enhanced due to a charge-permanent dipole interaction. [10-15]

(ii) Independently of the positions of the energy levels of the guest molecule with respect to those of the host, its permanent dipole moment locally modifies the polarization energy due to a contribution to the local field acting on a localized carrier, resulting in the appearance of local states in the vicinity of the dopant [16,17]. Calculations show that the depth and cross-section of traps formed in such a way depend not only on the dipole moment but also on interactions between dopant molecules.

The situation in disordered molecular solids is more complicated as their behaviour can seldom be correctly described within models developed for nearly-perfect single crystals. Here, basic ideas stem from the work of Bassler and his collaborators (see [18,19] and references therein) who put forward a model describing the transport of charge carriers in these systems. Principal results confirming the validity of this model have been been reviewed in several books and articles (see, e.g., [18-22]). The role of the polarity of dopants in disordered molecular materials has been discussed in several papers. Results obtained on molecularly doped polymers indicate that the presence of dipoles manifests itself in modifying the carrier mobilities. Systematic studies carried out by several researchers (see [23] for references) demonstrate that the polarities of both, charge transporting materials and the polymer binders modify the mobilities. The effect has been explained by introducing a dipolar contribution in tho the density-of states function [24,25].

Acknowledgement

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TIME-DOMAIN INVESTIGATION OF ORGANIC MATERIALS.

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The contribution is related to experimental studies of electrical properties of organic materials carried in time domain / TD/ as well as frequency domain /FD/.
Therefore, significant contribution to observed phenomena is due to charges, mobile or localized. In the materials in test ionic conduction seems to be natural one.
Numerous physical phenomena are contributing to sample response at elevated time of measurement. Time window of these experiments is from 10^{-4}s till hours or days. For frequency change, the window width is 10kHz - 10^{-4} Hz.
It is obvious, that dipolar effects are hardly to be observed in time /frequency range indicated above. These are as following: transport of charge, space charge polarisation, dissociation of neutral species (thermal and electric field enchanced), diffusion of neutral as well as charging species, carrier recombination and carrier emission from an electrode.
For reasons unknown to the Author last phenomenon is not taken into account in the case of ionic conducting materials.
For organic solids, particularly aromatic ones, peculiarities of electron transport were investigated in details. There are numerous models working satisfactory in this field. The case of ionic conduction is treated in the way similar to that of liquid or solid electrolytes, means , materials with high ionic concentration. The results related to ionically conducting media are considered in terms of electrochemistry, where water-containing media are of main interest. It is not the case considered here. In numerous organic materials, polymers particularly, ionically conducting impurities are present in different amounts. Therefore carrier concentration may vary significantly from high to very low. Introduced earlier Weak Electrolyte model fails in case of existence of interfacial phenomena.
For low carrier concentration charge screening length is large. Instead, one may take into account carrier solvatation, particularly important in polar materials. Solvatation may influence transport in considerable way.
Time domain experiments may give considerable input to the understanding of above

mentioned phenomena. Particularly it happens when interaction between electrode and material must be taken into account. These phenomena may produce nonlinearities difficult do deal with by means of FD. In water-containing materials electrode processes are linked to numerous chemical reactions. It is shown that in particular organic materials interference of chemical reactions can be ignored. Thus, electrode-material interaction can be elucidated, at least, in same part of it..

For considering of interfacial phenomena mutual relation of FD and TD data is of interest. The main point of equivalence of these methods is a statement of linearity of the response. However, this criterion is not well defined. Therefore it is of importance to relate results obtained in FD to TD ones. It can be shown in the text that they are not always compatible.

In the case of materials under test, time domain technique is giving an evidence of space charge polarisation and electrode emission phenomena. These phenomena are determining current-time response for elevated time. One may suggest a link of these currents to the earlier developed concept of Quasi-DC conductivity.

The discrimination between diffusion, dissociation and recombination is more speculative. Evaluation of the these mechanisms is related to the models available. However the development of these models are much inferior to FD case. It is the reason, why TD data are often transformed to FD data.

However, it is worth to note, that FD related models are macroscopic ones and contain little or any information related to microscopic level of the material.

Therefore, exploitation of TD data in full depends on further progress related to theoretical description of low-frequency electrical response of ionically conducting materials.

DIELECTRIC RELAXATIONS IN SIDE-CHAIN LC POLYMERS

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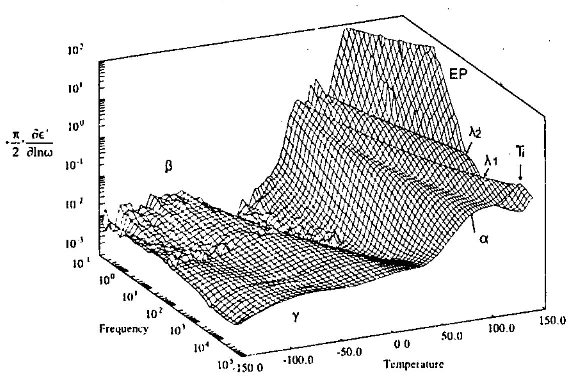
Side-chain liquid crystalline polymers (SCLCP) consist of linear polymer chains containing side groups with the common structure.
[flexible spacer]-[rigid mesogenic unit]-[flexible tail].
Such materials combine the mesomorphic properties of low molecular weight LC's with typical polymer properties. Although LC's and LCP's have many features in common, the introduction of a polymeric backbone results at least in two basic modifications:

1. The polymer chains organize themselves in a separate phase which may give rise to a superstructure on top of the mesogenic order (e.g. smectic layers).
2. The ordering and molecular motions of the mesogens are influenced by the long-range dynamics of the polymer backbone.

This paper focuses on molecular dynamics in side-chain LCP's with different chemical structures. The main technique used is dielectric relaxation spectroscopy (DRS), which is particularly sensitive to molecular motions involving polar groups. Its major advantage is the ability to cover a broad frequency range (typically 10^{-1} to 10^{6} Hz) at temperatures ranging from the glassy/crystalline to the isotropic state.

As a typical example of the complex relaxation behavior, the conduction-free „loss" spectrum of $\partial e'/\partial \ln w$ of a LC-polycarbonate[1,2] is shown in fig.1.



Apart from the electrode polarization (EP) and the isotropization temperature (T_i), three strongly coupled relaxations are clearly visible above T_g. They refer to the segmental backbone motion (a-process) and the rotational diffusion of the nitrostilbene mesogen (l_1, l_2-process). The three partially overlapping secondary relaxations below the glass transition temperature are attributed to local processes (g, b_M) as well as to highly co-operative hindered rotations involving the mesogenic unit (b_S).

The assignment of such complex relaxation processes, which also show up in LC-polyurethanes[3], polyethyleneimines, polysiloxanes and poly(maleic anhydride), was facilitated by a systematic *variation of the molecular structure* (spacer length, side groups, copolymers…) and the use of *advanced techniques* for the analysis and modeling of the dielectric spectra. Three evaluation methods will be discussed in this paper:

a) the elimination of ohmic conduction from loss curves using the Kramers-Kronig transform or by using Me'/Mlnw,
b) the calculation of the apparent,"local" activation energy as a function of both T and w,
c) two-dimensional fitting of the loss curves in the temperature and frequency domain.

Sub-T_g relaxations in LCP's (g, b) may be distinguished into two categories:

1. Processes involving polar groups of the backbone and other, mere local (thermally activated) motions in the side group.
2. Relaxations (b_S) within the frozen-in mesogenic order showing remarkable activation parameters.

Here we will focus on the properties of the b_S -relaxation, which turned out to be sensitive to the LC order.

Relaxations in smectic LCP's related to the glass transition are treated from the viewpoint of polymer dynamics modified by physical crosslinks. Possible origins for strong intermolecular interactions are:

a) nonpolar mesogens anchored in the smectic layer structure suggesting a relation between crosslink density and the order parameter ,
b) polar mesogens (e.g. nitrostilbene, cyanobiphenyl) tending to form pairs (dimerization) which may persist even in the isotropic state,
c) mesogene locked in a (2-dimensional) crystalline phase,
d) hydrogen bonds between different backbones (e.g. urethane-urethane bridges) or sidegroup-sidegroup/sidegroup-backbone bridges.

As for covalently bonded networks, each intermolecular bridge will decrease the mean flexible chain length resulting in a specific increase in the glass transition temperature and thus delaying the a-relaxation. Changes in the temperature dependence of the a-process (usually VFT-like) therefore indicate changes in the degree of intermolecular interaction as is well known from melting or the $S_m \rightarrow$ I transition. The role of H-bonds on the phase behavior in LC- polyurethanes will be discussed in some detail.

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RELAXATION OF COMPLEX SYSTEMS FROM LOCAL RANDOMNESS TO GLOBAL DETERMINISM.

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Empirical evidence accumulated over the years shows that the time-dependent change of macroscopic properties of physical systems evolving to equilibrium exhibits a great degree of universality. The nonexponential regression is observed in variety of problems from condensed matter physics, nuclear physics, spectroscopy, rheology, seismology, physical chemistry, molecular biophysies, cell and population dynamics, etc. The wide occurence of the Kohlrausch-Williams-Watts and Havriliak-Negami responses in fitting the relaxation data has led to a commonly accepted assumption about some universal pattern underlying the relaxation processes, which is independent of the details of individual systems.

In order to understand the phenomenon of the universal relaxation response one needs to consider relaxation of complex systems in a way that separates it from a particular physical context, and the observation that the dynamics of such systems is characterized by seemingly contrary states, i.e., local randomness and global determinism, is crucially relevant to this issue. Determinism appears via empirical laws, observed on the macroscopic level, while randomness is induced by variations in the local environment. These two states, in a natural way, can coexist in the framework of the limit theorems of probability theory when the relaxation function $\phi(t)$, being the survival probability of the system in the initially imposed nonequilibrium state until time t, is described by the first-passage of the system.

The universal pattern underlying the relaxation processes transpires from the fact that limit theorems give us strict constraints on the mathematical form of the first-passage relaxation function. Moreover, the derived formulas exhibit the properties of the empirically observed responses.

PULSED ELECTROTHERMAL TECHNIQUE FOR THE CHARATERIZATION OF DIELECTRIC FILMS

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The measurement of thin film properties of dielectric films used in microelectronic packaging or optical communication technology represents a challenging task: Methods allowing such measurements may prove to be useful for the in-situ characterization of films in practical device geometries.

The measurement of the electrical response of a dielectric material after a transient thermal excitation has proved to be viable for the determination of several material properties, such as the thermal diffusivity [1], elastic compliances, and piezo- and pyroelectric [2] coefficients. The thermal excitation is performed by the absorption of a short laser pulse in the top electrode of the thin film capacitor sample. Additionally, the technique allows for the high resolution probing of nonuniform dielectric feld or dipole polarization distributions across the thickness of the dielectric film [3]. By applying a dc-bias field, the technique is applicable not only to polar films, but also to any dielectric film, for example nonpolar polymers. Modifcations are required in order to allow for investigations of films with thicknesses of 1 μm or even below, as dictated by applications in microelectronics and optical communication.

In this paper several adaptations of the technique will be described, such as an extended set-up with a microscope heating stage allowing for temperaturedependent experiments. Additionally the spatial resolution for probing nonuniform field or polarization distributions has been enhanced by using wide bandwidth amplifiers and short ns-laser pulses. Employing currently available, small-scale laser systems a compact experimental set-up can be established.

The application of the technique will be demonstrated by representative examples: the determination of elastic, piezo- and pyroelectric properties of ferroelectric

P(VDF-TrFE) films, the determination of the thermal diffusivity of an amorphous, photonics polymer with chemically attached azo-dye chromophore dipoles deposited on highly thermally conducting silicon substrates, and the insitu determination of the polarization profile during heating a bimorph structure consisting of polar polymers with different glass-transition temperatures.

In 75/25 P{VDF-TrFE) copolymer films; thermally induced piezoelectric oscillations can be used for the determination of elastic and piezoelectric film properties in addition to the pyroelectric properties. The temperature dependence of the different properties has been analyzed especially in the vicinity of the glass-transition were marked changes are expected in the elastic properties.

The thermal diffusivity D, e.g. the ratio of the thermal conductivity k and the specifc heat cp D=k/cp of the photonics polymer has been determined in the vicinity of the glass-transition temperature T_g. Around T_g, a step-like change in the specific heat cp is expected and thus also in the thermal diffusivity. However, in the thin film investigated no evidence of the glass-transition is seen in D, which is related to the dynamic behavior of cp around T_g.

The last example shows the high spatial resolution obtained in mapping polarization distributions in a two-layer stack of polar polymers with different T_g's (Fig.1). Such step-like dipole orientation profiles are important in effcient modal-dispersion phase-matched second-harmonic generation [4].

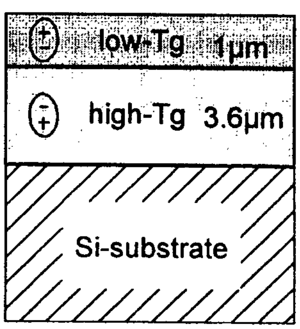

Fig.1.: Schematic view of the bimorph structure consisting of two polar polymers with different glass-transition temperatures (T_{g1} =140°C, T_{g2}=165°C).

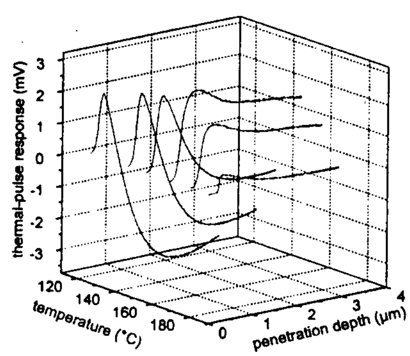

Fig. 2.: Temperature-dependent thermal-pulse response of the polymer stack shown in Fig.1.

Most notable is the change of sign in the thermal-pulse (TP) response of the polymer stack, as shown in Fig. 2. The signal has been scaled according to the transformation $x = \sqrt{2Dt}$, where t is the time after the thermal-pulse excitation and x is the thermal-pulse penetration depth. The transient response has been recorded while the polymer stack was heated at constant rate. At temperatures much below the T_g's of the polymers, most notable is the change of sign in the transient response when the thermal-pulse enters the low-T_g polymer layer, indicating a larger polarization in this polymer film. As the temperature increases, the dipoles relax first in the low-T_g polymer, and thus the TP-response stems solely nom the high-T_g polymer, e.g. no sign change is observed. Finally, the TP-signal drops to zero when all dipoles are relaxed.

The techniques described seem to be well suited for the investigation of different thin film polymer systems. he very high sensitlvity of the method may even allow for the investigation of films with thicknesses far below 1 μm, as is the case in electroluminescent polymer fiims or organic solar cells.

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THE CHECK OF THE STOKES-EINSTEIN-DEBYE DIFFUSION LAW IN EPOXIES OF INCREASING MOLECULAR COMPLEXITY

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The conductivity and relaxation time data of epoxy compounds having an increasing number of epoxy groups, from 1 to 3, were analysed to check the validity of the Stokes-Einstein-Debye diffusion law (SED). For mono- and diepoxide the prediction of the SED model was verified, while a breakdown of the SED relation, accounting for a decoupling between translational and rotational motions and well represented by a fractional power law (FSED), was observed in tri-epoxide for some tenths of degrees above the glass transition temperature. 'The transition between SED and FSED behavior is connected with the splitting between main and secondary relaxations and with the change of the main relaxation from a Vogel-Fulcher regime to another.

ON THE SCALING OF RELAXATIONAL PROCESSES

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During recent years much interest has been paid to the concept of the universal scaling ofthe α relaxation process in glass-forming liquids [1]. The most important feature of the suggested scaling procedure is related to the presence of the additional second power-law region above the peak in $\varepsilon''(\nu)$ of the α, process in many supercooled liquids. The scaling curve implies the relationship between the two high-frequency regions [2]. On the other hand, a number of authors have pointed out considerable limitations of the scaling procedure [3].

Recently, we reconsidered some of the formal aspects of the suggested scaling procedure and proposed a modified scaling relationship [4]. In the present paper we extend our analysis for the case of the conductivity relaxation process in ionic conductors (electric modulus representation). The relationship between the two high-frequency regions in the spectral shape of both processes is discussed.

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ISOTHERMAL AND NON-ISOTHERMAL RELAXATION PROCESSES IN DYE-DOPED POLYSTYRENE

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The build-up of a polarized state and its relaxational behavior in a NLO guest-host system obtained by doping of polystyrene (PS) with the disperse red 1 (DR1) dye molecules have been studied by different methods including the AC dielectric spectroscopy, the thermally stimulated polarization (TSP) and depolarization (TSD) currents, Hamon's method, isothermal absorption currents measurements. Thus, we were able to cover wide ranges of temperatures (from −160 to +130°C) and frequencies (from 10^{-5} to 10^{7} Hz). The 20 micrometer-thick samples were poled by either "sandwich" method, or in a constant current triode. Three TSD peaks observed at sub-zero temperature have been identified as related to beta-, gamma-, and ro-processes. The alpha peak was observed at dielectric loss curves with its position changing from 10 Hz at 100°C to 3×10^{4} Hz at 130°C and narrowing with temperature. Temperature dependence of the relaxation time agreed with the Williams-Landel-Ferry model. It was concluded that beta processes contribute to relaxation of a poled order in a sub-T_g range. Alalyzing isothermal polarization and depolarization currents we observed good agreement between experimental and calculated data even for a short poling time of 4 s, thus proving the validity of the superposition principle, although the response function deviated considerably from the usually stipulated power law. It has been found that position and appearance of the TSD peaks in "sandwich" poled samples depended on the poling temperature. The highest obtained polarization corresponded to 17% of the maximum theoretical value. The Willams-Watts model was applied to interpret TSP curves showing the characteristic behaviour of the beta component followed by a plateau and a rise near T_g typical for the alpha process. To apply the model for a non-isothermal case, we used a concept of intrinsic time suggested by Jonscher, DeBolt, van Turnhout, and Halpern. We have found that isothermal behavior did not fully determine the TSP results, probably because the dye molecule due to its big size needs large intrinsic

time to reach equilibrium, what is afforded in the isothermal but not in the TSP measurements. A specially designed corona triode was used in order to find how residual polarization depended on corona polarity, poling temperature, grid voltage, after-poling treatment and time of aging. The observed features of the TSD curves have been explained considering existence of the dipole polarization as well as the surface and space charge. The trapped charge was more stable than the dipole polarization, so that even the post-poling growth of polarization was observed in non-neutralized samples. The obtained results supplemented to our knowledge on mechanism of corona poling and provided data for optimization of the poling procedure.

DIELECTRIC AND LIGHT SCATTERING ANALYSIS OF MAIN AND SECONDARY RELAXATIONS DYNAMICS

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The dynamics of different epoxy compounds was studied by wideband dielectric spectroscopy and light scattering from below to above the glass transition temperature, T_g.

Evidences are given of a transition temperature located some tenths of degrees above the glass transition where a change in the temperature behavior of the main relaxation time, together with the splitting of the structural and secondary relaxations, occurs. For temperatures approaching T_g, a deviation from the Stokes-Einstein-Debye diffusion law is evidenced; it can be interpreted in terms of a correlation length for the structural relaxation which increases for decreasing temperature.

ISOTHERMAL CURING OF EPOXY RESINS AS SEEN BY DIELECTRIC, DIRECT-CURRENT AND TIME-OF-FLIGHT MEASUREMENTS

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The electrical techniques of monitoring of resin curing like dielectrometry (*ac*) and direct-current measurements (*dc*) attract increasing interest because it is believed, that they are able to control *in situ* the physicochemical changes in the reacting media. The basic assumptions in these techniques are that the ionic conduction is directly related to the medium viscosity *via* Stokes law and that the ion concentration is constant during the curing. On the other hand only few fundamental studies on the mechanism of ionic conduction in these materials have been reported. Therefore, the relationship between the evolutions of the ionic conductivity σ, viscosity η and the physicochemical changes in the polymer system is still not established.

In order to get better understanding of these correlations in the epoxy-amine reacting systems we have investigated the changes of the conductivity using both the *ac* and the *dc* techniques. Additionally, a new electrical technique was elaborated, basing on the Time-of-Flight (TOF) concept. This technique was used to determine the evolution of the ionic mobility μ in a course of the reaction [1]. The electrical and rheological experiments have been carried out in the epoxy-amine reacting systems that gelify and vitrify : diglycidyl ether of bisphenol A with diamino-4,4'-dimethyl-3,3'-dimethyldicyclohexylmethane (*DGEBA-3DCM*) or diglycidyl ether of bisphenol A with 4,4'-methylenebis[3-chloro-2,6-diethylaniline] (*DGEBA-MCDEA*) or in the reacting medium that gelify only : diglycidylether of 1,4-butanediol with 4,9-dioxa-1,12-dodecane diamine (*DGEBD-4D*).

It was found that the *dc* and *ac* methods yield similar results concerning the evolution of the ionic conductivity at the beginning of the reaction, up to an appearance of the relaxation processes related to the vitrification that affect strongly the *ac* measurements. The correlation between the ionic mobility and of the dynamic and static viscosity has shown that ionic mobility changes follow the Stokes' law at the beginning of the curing only. The evolutions of the ionic mobility and the viscosity can be better described by the empirical Waldens' rule, but this works only in the limited range before the gelation.

We have found also an inconsistency between the time dependences of the ionic conductivity and the mobility. This indicates that the concentration of the ionic charge carriers is decreasing with the advancement of the reaction. One of the possible reasons for that phenomenon can be the change of the relative dielectric permittivity of the reacting system and therefore of the dissociation constant during the reaction. The analysis of the shape of the Time-of-Flight peaks indicates also that the distribution of the ions in the sample volume is changing with an advancement of the reaction.

We conclude, that the measurements of the evolution of the electrical properties in reactive media can be applied for the *in situ* monitoring of the advancement of the reactions [2-3]. However, these methods can not be easy generalized for different systems and it is necessary to find the empirical relationships between the changes of the electrical parameters and the advancement of the reaction for each reacting system and for each curing condition.

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TO THE FRACTAL ORIGIN OF DIELECTRIC SPECTRA OF FERROELECTRICS

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The experimental investigations of the low-infralow-frequency dielectric spectra $\varepsilon^*(\omega)$ of the ferroelectrics and related materials brought to light the transformation of the type of dielectric response to another one under different conditions. The transformation takes place due to arising of the pre transition phenomena with aproaching the phase transition regions, due to variation of experimental procedure (frequency, elecric field intensity, rate of cooling or heating) and due to prehistory of a same (aging, annealing, *etc.).* One can reveal as low as a few types of the dielectric response which are common to dielectrics of different nature [1,2] (see Table).The fractional-power dependences of ε' and ε'' on frequency and time are unique to all of them that seems to be the general feature of the dynamic response of fractal systems. As it also appeared from experiments different types of dielecrtic spectra vary in self similar manner with temperature, electric field intensity and aging time.

The deviations from the Arrhenius-like behavior have been found for characteristic relaxation times of the Cole-Cole, Davidson-Cole, Havriliak-Negami, Williams-Watts dispersion types. For so-called linear dispersion types[2-6] (which are lines with positive, negative or zero slopes in a complex plane) the critical slowing has been found at structural and phase transition regions. The slowing down has character of the fractional-power dependence of the relaxation frequency on temperature
$\nu_r \sim |T-T_m|^z$ with T_m, close to phase transition temperature. We revealed the connection of the exponent z with the index of three-dimensional percolation model and with indexes of the dynamic scaling theory. It seems to be additional argument in favour of fractal origin of dielectric response of a matter.

We came to the conclusion that types of dielectric spectra owe their universality to the self similar motion of relaxing particals groups. As to ferroelectrics the analy-sis of the optical microscope researches brought to light the fractal features of domain boundaries and their temporal evolution[6]. Fractals which are the self similar or self affine objects are known as widely spread in nature[7]. The evidences of the fractal geometry of domains have been found through the evaluation of their fractal dimensionalities.

The irreversible thermodynamics equations modified by introducing of the fractional derivatives have been supposed for description of fractal systems consided in particular as biphase systems[8]. We describe the preponderance of the dielectric spectra, explain the critical slowdown of relaxation, find agreement with observed features of interfaces motion and fractal models.

The meaning of the derivatives of fractional order[9] has been discussed in Ref.[10-12]. We evaluated the dynamic fractal dimensionalities D from the dielectric spectra[6,8] and investigated their temperature dependences. Being approximately unchanged in some temperature intervals D-values sharply change at phase transition. The role of pre-history and existence of defects is very significant.

TABLE I. Typical dielectric spectra and fractional differential equations

Normalized dielectric spectra	Fractional different equations
$e^* = \left[1 + (i\omega\tau_\gamma)^\gamma + (i\omega\tau_\beta)^\beta\right]^{-1}$	$\left(1 + \tau_\gamma^\gamma D^\gamma + \tau_\beta^\beta D^\beta\right)\varphi = A'E$
$e^* = \left[1 + (i\omega\tau_\gamma)^\gamma + (i\omega\tau_\beta)^\beta\right]^{-\xi}$	$\left(1 + \tau_\gamma^\gamma D^\gamma + \tau_\beta^\beta D^\beta\right)^\varphi \varphi = A'E$
$e_\beta^* = (i\omega\tau_\beta)^{-\beta}$	$\tau_\beta^\beta D^\beta \varphi = A'E$
$e_\beta^* = (i\omega\tau_\varsigma)^\varsigma$	$\tau_\varsigma^{-\varsigma} D_t^{-\varsigma} \varphi = A'E$
$e^* = (\omega\tau_b)^{-\beta} - i\,\mathrm{tg}\,\delta_\infty$	$\omega^{-\beta}\left(1 + D^\beta\right)\varphi = CE(\omega)$
$e^* = (\omega\tau)^\gamma - i\,\mathrm{tg}\,\delta_s$	$-\omega^\gamma\left(1 + D^{-\gamma}\right)\varphi = BE(\omega)$
$e^* = \left[1 + (i\omega\tau_\alpha)^{1-\alpha}\right]^{-1}$	$\left(1 + \tau_\alpha^{1-\alpha} D^{1-\alpha}\right)\varphi = A'E$
$e^* = (1 + i\omega\tau_e)^{-\xi}$	$(1 + \tau_e D)^\xi \varphi = A'E$
$e^* = \left[1 + (i\omega\tau_\alpha)^{1-\alpha}\right]^{-\xi}$	$\left(1 + \tau_\alpha^{1-\alpha} D^{1-\alpha}\right)^\xi \varphi = A'E$
$e^* = \left[(i\omega\tau_\varsigma)^{-\varsigma} + (i\omega\tau_\beta)^\beta\right]^{-1}$	$\left(\tau_\varsigma^{-\varsigma} D^{-\varsigma} + \tau_\beta^\beta D^\beta\right)\varphi = A'E$

$$e_\alpha^* = (\varepsilon^* - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty),\ e_{\beta\alpha}^* = (\varepsilon^* - \varepsilon_\infty)/\varepsilon_\infty,\ e_\gamma^* = (\varepsilon_s - \varepsilon^*)/\varepsilon_s,\ \mathrm{tg}\,\delta_s = \varepsilon''/\varepsilon_\infty$$

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Dielectric Spectroscopy of some Electrolyte Solutions in Dimethylsulfoxide/Water Mixtures .

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Although dimethylsulfoxide (DMSO) is widely used in many application fields, the origin of its peculiar properties in the liquid state is a matter of continuing debate, in that respect resembling water. The DMSO molecule is highly polar, so dipole-dipole interactions are to be taken into account in the first instance, in contrast to the less polar water, where hydrogen bonding effects are predominating. Both liquids are often used as solvents for electrolytes. It seems worthwhile to study DMSO/water/electrolyte systems by a method such as dielectric spectroscopy, which 'observes' the dynamics of polar entities such as molecules as well as ionic aggregations.

We have studied various salts dissolved in DMSO/water mixtures over a wide frequency range in dependence on solvent composition and salt concentration. The binary solvent exhibits peculiarities in its dielectric spectrum which point to a nearly stoichiometric interaction which, however, does not appear to lead to longlived 'complexes'. Salt solutions show an additional relaxation contribution at lower frequencies, which is likely to be due to 'ion-pairs' in quite a broad sense, probably those involving solvent. Some critical considerations will be added concerning the interpretation of so-called 'ion-pair' relaxation times. It is interesting to note that a competition between ion/solvent and DMSO/water interactions can be inferred from the dynamic dielectric data. Those effects will be discussed with regard to the kind of salt dissolved.

DIELECTRIC BEHAVIOR OF FERROELECTRIC LIQUID CRYSTALS IN THE VICINITY OF THE TRANSITION INTO THE HEXATIC PHASE

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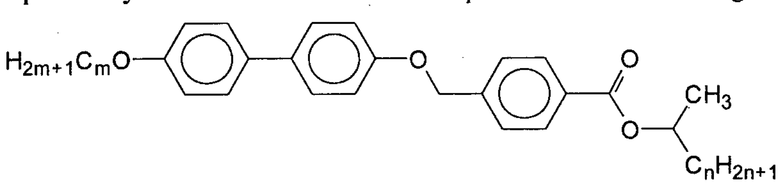
Hexatic smectic liquid crystalline phases exhibit a quasi two-dimensional (2D) structure characterized by a long-range three-dimensional (3D) bond orientation order and a short-range translational order, which extends a few hundreds Angströms within a smectic layer but one order less between them. When the material is composed of chiral molecules the tilted hexatic phases SmI* or SmF* are ferroelectric both and exhibit the same symmetry C_2 as the high temperature ferroelectric SmC* phase. The transitions SmC* - SmI* or SmC* - SmF* are of the first order without any symmetry change.

Collective molecular dynamics was studied in ferroelectric smectic C* and hexatic smectic I* phases by dielectric method with compounds from a homologues series



In the frequency range 1 Hz to 10 MHz one relaxation process was observed in both phases. In SmC* phase the relaxation frequency of this process linearly decreases and its dielectric strength slightly increases when approaching the SmC*-SmI* phase transition temperature T_I. In the SmI* phase the relaxation frequency is one order of magnitude lower and further slightly decreases on cooling (see Fig. 1).

A phenomenological theory has been developed, which describes static and dynamic dielectric properties near T_I and satisfactorily explains the experimental results[1]. The order parameters appropriate for the description of the SmC*-SmI* phase transition are bond orientation, tilt angle and polarization. The theory is similar to the mean-field approach applied in Refs. [2, 3], but moreover, the coupling with the polarization is taken into account for description of dielectric properties.

The observed relaxation has been attributed to fluctuations of the bond orientational order coupled to the molecular tilt. A parameter describing the softening of this mode has been determined by fitting theoretical results to the experimental data. The drop of f_r at T_I gives a ratio of the amplitudes of the bond order at T_I.

The spontaneous polarization, P_S, and spontaneous tilt angle, θ_S, have been measured with the same compounds. P_S exhibits a steep increase in the phase transition region, while θ_S only slightly linearly increases on cooling. The model [1] describes observed anomalous increase in P_S as a result of the jump up in the strength of bond orientational order when passing to the SmI* phase.

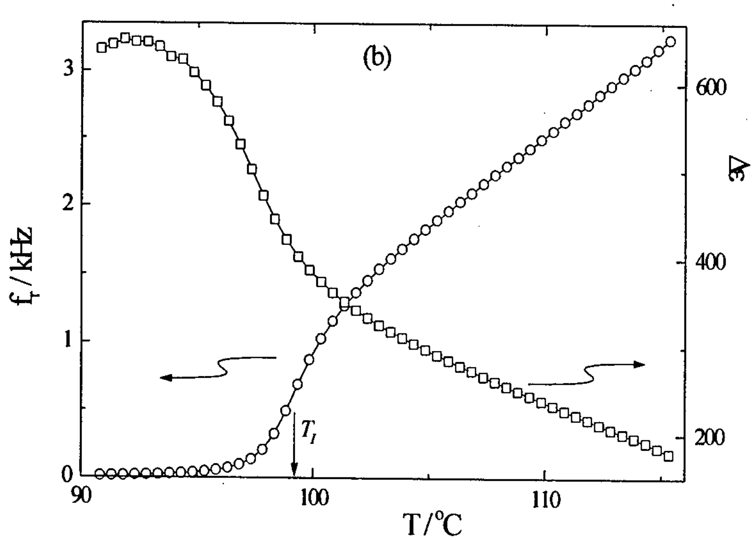


Figure 1 Temperature dependence of the relaxation frequency and dielectric strength of compound m=14, n=6. The arrow indicates the temperature T_I of the SmC* - SmI* phase transition as determined from DSC.

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THERMAL AGEING OF PYROELECTRICITY IN PVDF AND P(VDF-TrFE) COPOLYMERS

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Since the discovery of strong piezoelectricity and pyroelectricity in Poly VinyliDene Fluoride (PVDF) and the improved processing of P(VDF-TrFE) copolymers with respect to PVDF, the use of these materials for the development of sensor applications has been continuously increasing. The structure and the electrical properties of this class of polymers have been a subject of great interest over the last years. It has been clearly demonstrated that the ferroelectric behaviour of these semi-crystalline polymers is responsible for their electro-active properties. Nevertheless, the complex mechanisms that induce the pyroelectric effect are not yet clearly understood.

It appears clearly that the dipolar contribution (dipolar libration, dipole moment variations) is not sufficient to explain the temperature dependence of the pyroelectric activity. Indeed, variations of the sample dimensions and reversible crystallinity changes play a non negligible role in pyroelectric effects. Up to now, the relative contributions of these different contributions have not been clearly determined. The study of the evolution of the pyroelectric coefficient as a function of temperature contributes to improve the understanding of this complex behaviour. Moreover, the evolution of the pyroelectric activity after annealing at relatively high temperature is of a great interest for this field of investigation as well as for practical purposes.

The results reported in this work were obtained on commercially poled ferroelectric films of bioriented PVDF and P(VDF-TrFE) 75-25 mol.%, supplied by Solvay. The analysis of pyrocurrent spectra has been carried out in a large temperature range of -100°C up to +140°C. Dilatometry measurements and ThermoStimulated Currents spectroscopy have been used as complementary techniques of investigation.

In order to record the pyroelectric current spectra, metallized samples were placed between electrodes short-circuited under a high sensitivity ammeter. The samples were submitted to constant heating/cooling rates. In this way, the pyrolectric coefficient was directly deduced by dividing the pyroelectric current by the temperature variation rate and by the sample area. The pyroelectric coefficient shows a distinct temperature dependence below and above thermal transitions, and especially the glass transition.

We considered how this dependence changes upon thermal ageing. The influence of both ageing temperature and ageing time were investigated.

The annealing temperature was varied from +50°C up to +150°C, while the ageing time was varied from 30 seconds up to 100 hours. Experimental results show that the decay of the pyroelectric activity is apparently linearly dependent on the annealing temperature. The evolution of the decay of pyroelectricity as a function of the ageing time is more complex. Indeed, the pyroelectric coefficient decreases quickly below a short ageing time (a few minutes), and much slower at longer times. This characteristic time is ageing temperature dependent. Although P(VDF-TrFE) 75-25 exhibits a Curie transition at the temperature of +130°C, identical ageing conditions induced a lower decay of pyroelectricity in this material than in PVDF which does not undergo a Curie transition below the melting point of ≈+170°C.

It is now assumed that secondary pyroelectricity and volumic effects take a more prominent part in the pyroelectric effect above the glass transition than below the glass transition. Indeed, as primary pyroelectricity is not expected to undergo a specific variation at the glass transition, the important increase observed in the pyroelectric coefficient above Tg arises necessarily from other contributions. Hence, a parallel study of the evolution of the pyroelectric coefficient below and above the glass transition temperature might allow to estimate the relative contribution of the different mechanisms.

Dilatometry measurements have been performed in the same temperature range in order to determine the variations of the thermal expansion coefficients as a function of ageing conditions. This allowed to evaluate the influence of the variations of the sample area on the pyroelectric activity and on the decay of the pyroelectric activity. Comparison was made with the work of Kolbeck [1] who correlated the decay of piezoelectricity to the macroscopic shrinkage in case of oriented PVDF films.

Finally, the recording of ThermoStimulated Current spectra allowed to determine the influence of the ageing conditions on the relaxation modes. We have paid a particular attention to the evolution of the relaxation processes associated with the glass transition and with the a_c transition. The evolution of the dielectric manifestation of the glass transition on TSC spectra allowed to detect irreversible variations of the sample crystallinity. Besides, the a_c transition seems to play an important role in the ageing of pyroelectricity at least for PVDF film samples since any loss of pyroelectric activity was detected after ageing at temperatures lower than the a_c transition.

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DIELECTRIC RELAXATION OF 6-CB DISPERSED IN POLYMER MATRIX

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Liquid crystals of low molecular weight dispersed in a solid polymer matrix, are a new class of composites which can be used in different types of displays, switchable windows and other electro–optic devices [1,2]. Since dispersion of a liquid crystal in polymer leads to a large surface-to-volume ratio, the electro-optical properties of the polymer dispersed liquid crystal (PDLC) films are essentially determined by the interactions between the liquid crystal and polymer. On the other hand, the PDLC composites are heterogeneous and the interfacial effects are also of great significance. Due to the structural peculiarities of PDLC films, one can expect an essential difference in the physical properties of these materials and pure liquid crystals, especially - the dielectric properties measured in alternating electric fields.

Here we present the results of the dielectric absorption studies performed for the PDLC films consisting of the nematic 4-n-hexyl-4'-cyanobiphenyl (6-CB) dispersed in the polyester resin matrix (20, 30 and 40 weight % of 6-CB).

The main conclusion arising from our results is: in the nematic droplets of 6–CB dispersed in the polymer a part of molecules behave as in pure 6–CB. These 'free' molecules, situated at the centre of droplets, are not affected by the anchoring forces. The important problem: what is the proportion of the number of 'free' molecules in respect to the total molecules number in droplets can be quite easily resolved here, because the ratio of the dielectric strengths A_l obtained for the droplets and pure 6-CB gives directly the proportion in question. From our estimations results that the fraction of the 'free' 6-CB molecules in the nematic droplets amounts about 10%, independently of the nematic contents in the PDLC films.

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DECAY OF FREE ELECTRON-HOLE PAIRS IN DIAMOND-LIKE CARBON THIN FILMS

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1 .Introduction

Numerous physical properties of diamond-like carbon (DLC) have been studied thoroughly during the last decades due to their foreseen practical applications. The life-time of charge carriers is one of important physical quantities describing the transient behaviour of semiconducting or insulating material. In this paper the charge carrier life-time in DLC thin films is studied using two different experimental methods.

The first method is based on measurements of the frequency dependence of capacitance and dielectric losses of rectifying junction under the forward-bias voltage. The real (C') and imaginary (G/ω) part of the complex capacitance for a forward biased rectifying junction are given by [1] :

$$C = \frac{G_0\sqrt{\frac{1+\omega^2\tau_c^2}{2}-\frac{1}{2}}}{\omega} \qquad (1)$$

$$\frac{C}{\omega} = \frac{G_0\sqrt{\frac{1+\omega^2\tau_c^2}{2}+\frac{1}{2}}}{\omega} \qquad (2)$$

Fig. 1 shows the spectral shape of both the capacitance C and G/ω for the life-time equal to $\tau_c=10^{-3}$ s. This capacitance under the forward bias voltage is called the diffusion capacitance. The response shown in Fig.1 relates toa perfect junction. In case of real junctions the dielectric response may differ from the one shown in Fig.1 due to trapping phenomena which often take place in real junctions.

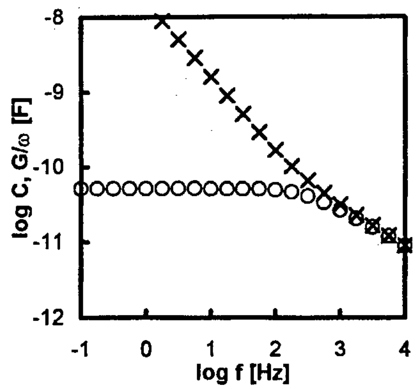


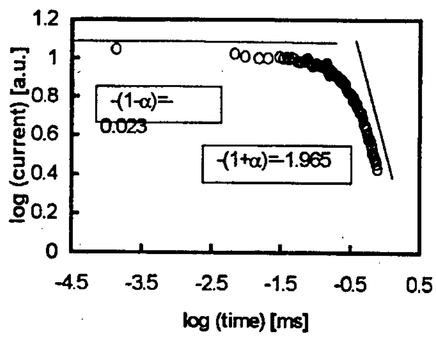
Fig. 1. The spectral shape of the dielectric response of p-n junction under the forward bias.

The second method consists in measuring the time decay of transient currents resulting from optical uniform excitation of excess charge. For the disordered systems, the pulse often consists of two parts of different slopes in the double logarithmic scale. The slopes of the two parts add up to -2 for the classical case of the dispersive transport. [2, 3, 4]. The current pulse may be then described by:

$I \propto t^{-(1-\alpha)}$ for time shorter than t_r (3a)

$I \propto t^{-(1+\alpha)}$ for time longer than t_r (3b)

Where tr is the recombination time. The relations hold for the generation time much shorter than the recombination time. The time relating to the intersection of the two straight lines corresponds to the recombination time.



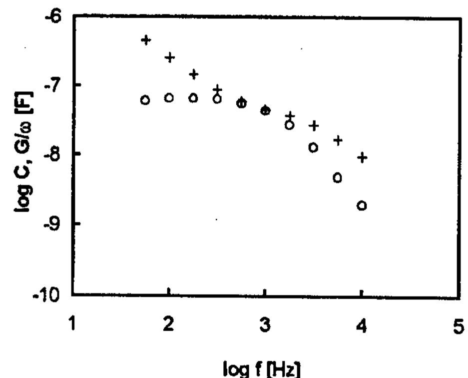


Fig. 2. The decay of transient current in a DLC thin film.
Fig. 3. The dielectric response of DLC/n-Si rectifying junction, 3V forward bias.

2.Results and Discussion

The decay of photo-current in DLC fihns (Fig.2) may be well described by expressions (3) for αclose to unity. The slopes of the two curves obtained for the voltages 5 V and 20 V sum up to about -2 and the time corresponding to the intersection has turned out to be independent of the voltage which confirms the suggestion that the time is related to the life-time of charge carriers. The value of the life time may be estimated to be about 0.3 ÷ 0.4 ms. In general the life time of charge carriers at the surface and deep in the film need not be exactly the same. Taking into account the geometry of the system it may be suggested that the processes close to the surface play a significant role in our case.

Fig.3 shows the dielectric response of n-Si/DLC rectifying junction under 3 V forward bias. This increase in capacitance seems to be quite typical of p-n junctions due to the so-called diffusion capacitance. The difference between the ideal curves shown in Fig.1 and those in Fig.3 may be due to trapping phenomena at the surface of DLC layer. The value of life-time of charge carriers estimated from Fig. is about 3 ms.

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DYNAMICS OF THE AFLC MOLECULES OBSERVED BY DIELECTRIC, ELECTRO-OPTICAL RESPONSE AND TIME-RESOLVED FTIR SPECTROSCOPY

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Broad band dielectric (10^{-2}- 10^{9} Hz) and electro-optic response (10^{-2} – 10^{5} Hz) have been studied for AFLC samples in antiferroelectric SC_A*, ferrielectric SCγ* and ferroelectric SC* phase as a function of temperature and d.c. bias freld. There are at least tree relaxation processes in SC_A* phase. Higher &equency relaxation processes, at 10^{6} Hz and 10^{8} Hz are certainly be assigned to the molecular reorientation around the short and long molecular axis. In addition, another two relaxation processes appear at 2-6· 10^{4} Hz and 4· 10^{3} Hz. The first one is attributed to the distortion of the antiferroelectric order in adjacent smectic layers, second exist only in the absence of d.c. field. In ferrielectric SCy* phase and ferroelectric SC* phase two collective modes exist. The process centred at 4· 10^{4} Hz is likely to be attributed to antiferroelectric coupling. For the molecule with the fluorinated chain the azimuthal mode is observed at reasonably low frequency $f \approx 1$ Hz due to the large moment of inertia of the molecule. Time-resolved IR spectroscopy have been used for studying the dynamic of the different segments of LC molecules. The result have been compared with those obtain by means of dielectric and electro-optic response.

SILICA XEROGEL INVESTIGATED BY THE METHOD OF THERMALLY STIMULATED CURRENTS

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Porous structure of SiO_2 xerogels obtained by the sol-gel method [1] has been investigated. Schematic illustration of this structure, with peripheral molecular layer in silica pores and molecular bridges linking fragments of xerogel, is shown in Fig.1. Medium pore radii ($\bar{r} = 2\,\text{nm}$) and strongly developed specific surfaces ($S = 680\text{-}730\ m^2/g$) are important macroscopic parameters characteristic of the investigated silica xerogels. The physical properties of xerogels also depend on the molecular state of pore surfaces and the bonds that create bridges linking particular silica fragments into a porous structure. The major influence of the state of internal surface on electrical conductivity of SiO_2 xerogels has been described in paper [1], while the role of molecular bridges in the processes of ion transport inside xerogels has been discussed in paper [2], where the influence of high pressure on electrical conductivity of SiO_2 xerogels has been examined.

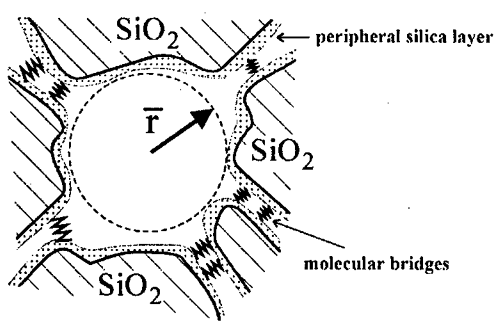

Fig.1. Porous structure of SiO_2 xerogels. Peripheral silica layer forming the surface of the pore and molecular bridges linking silica fragments are marked. The average pore radius is $\bar{r} = 2\,\text{nm}$.

Internal surfaces of SiO_2 xerogels have been investigated so far in terms of NMR studies [3], infrared [1, 4] and Raman [5] spectra. Those measurements indicate the presence of weakly and strongly bonded H_2O molecules and OH, Si-OH and Si-H groups on the surface of pores.

The purpose of this work was to investigate the internal surface of silica xerogels using relaxation spectroscopy. In particular, thermally stimulated depolarisation currents (TSD) in SiO_2 xerogels have been measured (Fig.2). Dipolar character of TSD spectra has been observed. Energetical analysis of these spectra has proven that the global TSD peak is formed by the superposition of several relaxation processes with activation energies in the range of 0.45 – 0.85 eV. Some samples were additionally heated in vacuum. Comparison of TSD spectra of heated and standard samples has proven that the $I_{TSD} = f(T)$ dependence reflects the molecular state of the internal surface of investigated silica xerogels.

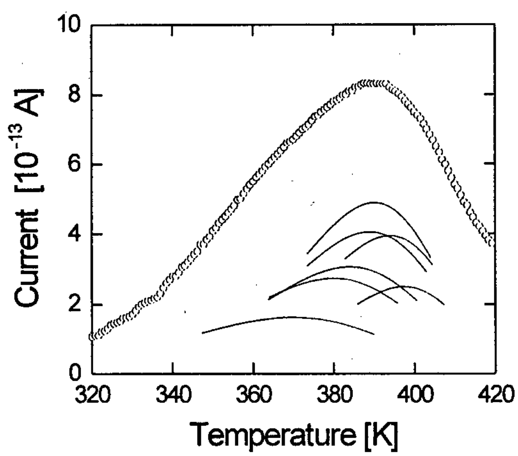

Fig.2. Global dipolar TSD spectrum of silica xerogel. The maxima of single relaxation processes forming the global spectrum are shown inside.

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LOW-FREQUENCY SCANNING CAPACITANCE MICROSCOPY

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The operation principle and main properties of the low-frequency Scanning Capacitance Microscope (LF-SCM) is described. The main attention is focused on its lateral resolution, signal-to-noise ratio and the possibility to detect dielectric losses.

Mapping the electrostatic field of a shielded microscope probe was used to calculate the stray capacitance, flux density, sensitivity and contrast obtained on a flat conducting surface, as well as on a surface covered by a thin dielectric film. The effect of dielectric losses, represented by a parallel conductance, on the detected capacitance and the resulting phase shift has been derived.

Using the results of mapping, the requirements on a SCM input stage and the possible solutions are discussed. From the point of view of frequency range and noise the best is an electrometric input stage, with input impedance represented by its capacitance.

The achieved signal-to-noise ratio renders the extension of the working frequency range to lower frequencies, offering the possibility of local impedance spectroscopy in the frequency range from about 1 kHz to a few MHz.

STUDY OF INVERTED MICELLES BY LINEAR AND NONLINEAR DIELECTRIC SPECTROSCOPY

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Inverted micelles are spherical structures built with amphiphilic monomers in nonpolar solvents, which have the possibility to encapsulate polar molecules. Dielectric spectroscopy is a good technique to study the dynamics of such supramolecular entities. Processes such as orientation relaxation, shape fluctuation and interfacial polarization cause increments in the permittivity which show relaxation in function of the frequency. By using a strong electric field, molecules with a dipole moment can lower their energy by realigning in the direction of the field. Another way to decrease their energy in the high field is by increasing their dipole moment through chemical reaction. This is the fundamental of a chemical perturbation technique whereby nonlinear dielectric effects (NDE) are measured in function of the frequency. The NDE is defined as the difference in perrnittivity at high and low field conditions. The most important contributions to the NDE are the Langevin saturation (due to reorientation of the rnolecules) and the anomalous saturation (due to chemical perturbation).

Two methods are developed for measuring the NDE, each with its own frequency range. They are both based on monitoring the field-induced changes in the parameters of a resonant system. For measuring between I and 100 MHz an LC-resonant circuit is used [1] and between 0.1 and 3 GHz a partially coaxial resonant cavity is utilized [2] . By changing the coil of the LC circuit or the length of the cavity it is possible to measure at different frequencies.

Linear and nonlinear dielectric spectra are measured for the system AOT (sodium-bis-2-ethylhexyl-sulfosuccinate) in cyclohexane between 6 and 45°C and for concentrations between 0.02 and 0.1 M. No extra amounts of water were added to these solutions. A very good agreement between the linear and nonlinear dielectric spectra is observed. It will be shown that the aggregation number of the micelles and their dipole moment can be calculated by combining both spectra. In this analysis we

find no room for the long-standing interpretation of Eicke et al. who used an inappropriate equation to fit their
data to construct a kinetic model for inverse micelle formation [3]. Finally, with linear dielectric spectroscopy the influence of added water on the dielectric measurements is investigated.

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SPACE CHARGE DYNAMICS IN DISORDERED DIELECTRICS

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Organic disordered materials play an increasing part in the wide field of dielectries. In particular, polymers are advanced materials applied in a large scale for insulators (cables), dielectrics (capacitors), electret applications (microphones) and in the electrophotography. For the understanding of these electrical properties the structure property relationship bas to be know.

In contrast to ordered solids, the structure of the disordered organics is rather difficult to describe in a quantitative way. Additionally, we have to take into consideration spatial inhomogeneitics, which is an unsolved problem until now.

For the electrical propertics of disordered organic dielectric materials, the consequences of the defect structure can be transformed in the electronic gap structure of the material. The electrical propertics of such materials at room temperature (T >> 0 K) have to be described as a charge carrier hopping transport. That means the electronic gap structure and the hopping rate definites the space charge evolution process inside of the material.

Also the transport of charge carriers in organic dielectrics can be described at a microscopic level by a hopping transfer on a lattice of sites. When multiple occupations of sites are forbidden the time evolution of an ensemble of interacting charge carriers can be rigorously described by the dynamics of an exclusion process. On much longer time and length a process of "aerating" takes place, so that the complicated microscopic structure of transport dynamics is replaced by a macroscopic drift–diffusion–equation.

On the basis of the stochastic theory of exclusion processes a microscopic description of the charge carrier hopping transport on localised states in disordered solids is given in [1] considering energetic and spatial disorder. A large time–space scale limit leads to a macroscopic charge transport equation (non–linear partial differential equation).

For disordered systems there are substantial difficulties to overcome in order to be able to analyze rigorously a transition from microscopic to macroscopic level.

In general, the large scale problem for disordered lattices cannot be solved by a closed formula for the macroscopic transport coefficients.

The aim is to describe the space charge evolution processes, that means to calculate the macroscopic transport coefficients (diffusivity, conductivity and mobility) in terms of the microscopic parameters (concentration and distribution of localized levels in the gap).

Using definite boundary and initial conditions the transport equation developed in [1] can be solved numerically and allows the calculation of important observables. A very useful observable both from the scientific and technological point of view is the surface potential and its kinetics. Therefore, the surface potential kinetics is discussed thoroughly in dependence on material parameters, film thickness, and surface charge. Furthermore it could be calculated the space charge evolution process, the conductivity, transit time and the concentration of localized states. The interpretation and the numerical solution of the presented transport equation give a new insight in fundamental problems of charge carrier transport in disordered materials. In particular, in this model both the disordered material and hopping rates are allowed to be spatially inhomogeneous at the large space scale [2]. For the first time a macroscopic drift–diffusion equation, including the spatial inhomogeneities of the material, could be derived. The equation has several drift forms caused by the spatially inhomogeneitics. The assumption of the principle of a detailed balance for hops between the localized energy states will play a crucial role for derivation of this transport equation.

The specific aspect of inhomogeneities will be demonstrated for special examples.

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METASTABLE ELECTRONIC STATES IN POLY(METHYL PHENYLSILYLENE)

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Amorphous silicon is a good semiconductive material for the fabrication of light-sensitive devices. It is a member of the large class of silicon compounds which encompass silicon clusters, silane oligomers, poly(siloxanes), and poly(silylenes). The last mentioned polymers are of considerable interest because of their unusual electrical, photoelectronic, and non-linear optical properties which follow from the effect of σ-electron delocalization along the chain [1]. Optical and electrical properties of these linear polymers have been found to differ significantly from structurally analogous carbon-based σ-bounded systems, resembling rather fully π-conjugated systems, like polyacetylenes.

The effect of photoinduced metastability has been known among inorganic amorphous photoconductors for many decades. The most prominent example was the metastability of chalkogenide glasses observed as the shift of the absorption edge after irradiation [2]. Later, Stabler and Wronski [3] observed reversible changes both in dark conductivity and photoconductivity in amorphous silicon. Similar effects can be expected in one-dimensional silicon polymers. Because this fact should strongly limit respective applications, the knowledge of the physical background of the metastability seems to be important. Here, we present some results obtained on prototypical material, poly(methyl phenylsilylene) (PMPSi).

The backbone photoexcitations in PMPSi around 3.5 eV are connected with σ-σ^* optical transitions; the absorption is broad and featureless, probably due to many conformational degrees of freedom of the chains. Photosensitive chromophores in side groups can be excited too [4,5]. The photogenerated electron-hole pairs or bipolarons with a short separation distance, formed in consequence of σ-σ^* electronic transitions on the same polymer backbone, recombine geminately very fast and principally do not contribute to the photocurrent. It follows from microwave photoconductivity experiments that lifetime of the pairs is shorter than 70 ns. A long distance intramolecular or intermolecular charge transfer is necessary to form an intermediate stage of more stable ion-pairs. The lifetime of the ion-pairs was detected to be several tens of microseconds [6,7], using the flash photolysis and microwave photoconductivity technique. The ion-pairs can dissociate in an external electric field forming thus free charge carriers. The dissociation process can be described in the framework of the Onsager theory [8]. The photogeneration efficiency increased in the presence of acceptor additives.

Polysilylenes seems to be good charge carrier transport polymers with field-dependent charge carrier mobility of order 10^{-8} $m^2V^{-1}s^{-1}$ (PMPSi, room temperature, $F = 3 \times 10^7$ Vm^{-1}). The zero-field activation energy of the mobility (PMPSi, 0.29 eV) consists of the polaron binding energy term and the distribution of transport hopping sites in energy [9]. The width of the distribution of electronic tail states was determined from the shape of the photocurrent pulse in the post-transient region [10] as well as from thermostimulated luminescence at low temperatures. Deep-charge carrier trapping is weak. However, a strong UV excitation of the polymer backbone led to the chemical bond scission and the formation of traps 0.45 eV deep with the frequency factor 10^{10} s^{-1}. It follows from the low stability of backbone negative polaron. This process was reversible, the reverse reaction could be accelerated thermally. A detailed analysis of post-transient photocurrent signal allowed us to estimate the changes in the density-of-states function (DOS) during the photodegradation. Our results are in agreement with the observations obtained using light induced ESR technique [11]. The light-induced centres formed during low photoexcitation intensities were ascribed to the Si skeleton stretching forces, creating weak bonds on backbone, acting electronically as trapping centers for the photoexcited charge carriers.

The total TSL intensity as well as time-of-flight photocurrent signal was drastically reduced with UV-irradiation exposition. The effect of annealing of the photocreated changes could be fitted by the relation ~ 1-exp $(-t/\tau)$, where t is time and τ is a time constant of the dissipation of quenching of TSL intensity or photocurrent. The time constant comprised 32.5, 5.6 and 1.6 h for the annealing temperatures 290, 315 and 330 K, respectively, giving thus the activation energy of the annealing process ~ 0.65 eV. This value is a typical value for unfreezing molecular motions as well as molecular diffusion in organic solids. In the case of a moderate photodegradation of PMPSi film (total TSL intensity is only twice decreased), the thermal annealing manifests a complete reversibility. In the case of strong photodegradation at room temperature (TSL intensity is about tenfold decreased), the annealing did not lead to complete recovering of TSL and collected photogenerated charge; the recovering is on about 30% level only. The time constant of the recover of TSL intensity during the annealing at room temperature was close to the value obtained from the photocurrent transients [12].

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OBSERVATION OF THE COPPER IONIC MIGRATION IN THE INSULATION LAYER BY A PULSED ELECTROACOUSTIC METHOD

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Metal-base printed wiring boards(metal-base PWB) have been applied to 100-400V power circuits for general purpose inverters and power transistor modules because of their high heat dissipation performance. Metal-base PWB generally constructed with a aluminum base plate, a thin insulation layer made of an epoxy resin with inorganic fillers and a copper conduction foil. In such metal-base PWB, the insulation layer is stressed under a high strength electric field of 1-3kV/mm, the reliability of the insulation layer is very important. With a large quantity of ionic impurities include in the insulation layer, the copper ionic migration from a copper conduction foil(anode) to a aluminum base(cathode) was observed by a scanning electron microscope(SEM) and an electron probe X-ray micro-analyzer (EPMA)[1]. However, non-destructive observation of a cooper ionic migration in the insulation layer have not yet been studied as between the conduction foils on the surface[2].

The space charge measuring technique has been improved and applied for the evaluation of insulating materials for high voltage apparatus. A high resolution space charge measurement system with a spatial resolution of about 10μm using the a pulsed electroacoustic(PEA) method has developed and reported[3]. The system measures the distance between an electrode and internal space charge in a sample with 150μm thick.

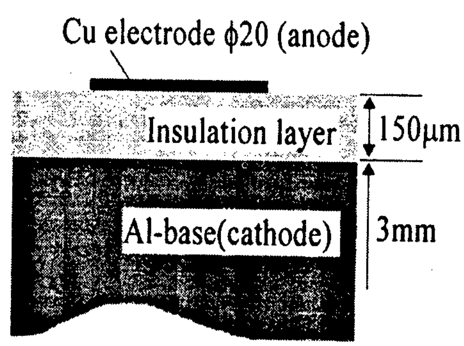
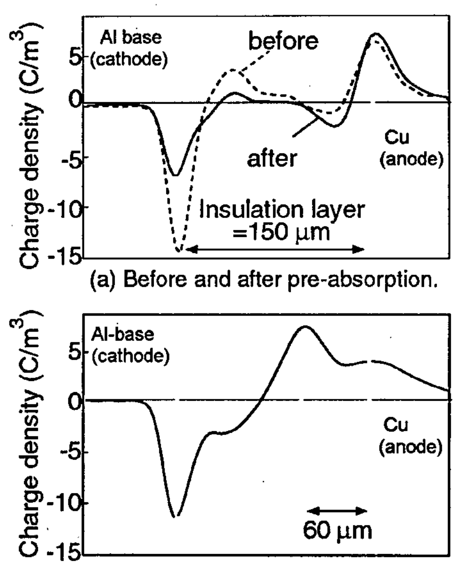


Fig. 1 Test specimen

Therefore, we have studied non-destructive detection of the copper ionic migration in an insulation layer of metal-base PWBs by a PEA method.

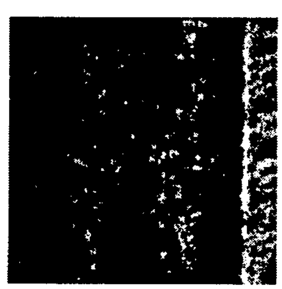
Fig.1 shows a test specimen. Copper electrode is coated to form a circular 20mm in diameter by vacuum evaporation. The 150μm thick insulation layer is an epoxy resin with inorganic fillers. The metal base is an aluminum plate 3mm thick. Before the enhanced thermal humidity bias(THB) test, the specimens were left for 18 hours in a chamber at 85 °C and 70%RH(pre-absorption) and then a voltage of DC1250V was applied to them for 48hurs. Charge distribution was measured by the PEA system at room temperature under application of 1250V.



(a) Before and after pre-absorption.

(b) After 48 hours applied DC 1250 V.

Fig.2.(a) shows the charge distribution before and after pre-absorption. The charges on both the electrodes and internal charges near the electrodes reveal as a clear peak. Since the internal charges were localized near the electrodes which have opposite polarity, the internal charge must be due to ions initially included in the insulation layer. Fig.2(b) shows the charge distribution after 48hours THB test. The positive charges were formed at a distance of around 50μm towards the cathode. In other words, the anodes seems to move 50μm towards the cathodes. Fig.2(c) shows the copper element distribution of the cross section of insulation layer using an EPMA. Copper element appeared inside the insulation layer. The region was the same as that



with positive charge shown in Fig.2(b). Therefore, the positive charge distribution near the anode is a conductive area due to copper ionic migration.

Conclusion of these experiment result, the growth of the copper ionic migration inside the insulation layer of the metal-base PWBs has non-destructive detected by means of the PEA method.

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MOLECULAR DYNAMICS IN ANISOTROPIC COMPOSITES BASED ON LC CELLULOSE DERIVATIVES

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Several cellulose derivatives (CD) form lyotropic solutions in acrylic monomers like acrylic acid (AA) or methacrylic acid (MAA). It makes possible creation of anisotropic composites with frozen mesophase by photopolymerisation of the acrylic monomer contained in the oriented systems. By proper choice of the cellulose derivative (length of side chains, kind of side groups) we have composed several pairs of the polymers with different intermolecular interactions. The (hydroxypropyl)cellulose (HPC), which have hydroxyl groups, can form with poly(AA) or poly(MAA) hydrogen bonds. In the case of the composites of the (cyanoethylpropyl)cellulose (CEPC) with the polyacids the dipolar interactions are possible due to highly polar CN groups, and in the case of the composites of the (propionyloxypropyl)cellulose (PPC), or the (hexanoyloxypropyl)cellulose (HxPC) with the polyacids only dispersive interactions are present. For all of the polymer pairs we have prepared two compositions, for which the mesophase is formed (60 % wt. and 40 % wt. of the CD), and one below the critical concentration (20 % wt. of the CD).

The interactions between polymer chains influence strongly the molecular dynamics of the systems. The molecular relaxation processes in the cellulose derivatives and in their composites were studied by the dielectric spectroscopy and complementary by the dynamic mechanical analysis (DMA). The investigated cellulose derivatives have glass transitions below room temperature and these transitions are seen in the dielectric spectra as a-relaxations. In the same temperature range pure poly(AA) and poly(MAA) have b-relaxations. The temperature dependences of the a-relaxations of the CDs follow the free volume theory (WLF) while for the b-relaxations of the polyacids the dependence is Arrhenius type. In the dielectric spectra the a-relaxations of PPC and HxPC are preserved also in the composites and the intensities of the loss maxima reflect the composition; the b-relaxations of the polyacids are masked by the a-relaxations of the CDs. Very different situation is for the composites with HPC and with CEPC, where the a-relaxations of the CD components are damped in a presence of the poly(AA) or the poly(MAA). In the case of CEPC composites the a-relaxation of CD is still strong enough to overlap the b-relaxation of polyacid, but the values of the dielectric constant (e') and of the dielectric loss (e") are much lower than one should expect from the compositions. The WLF parameters for the a-relaxations of the CD in the composites with the mesomorphic organization (*i.e.* containing 40 % wt. or 60 % wt. of CD) are not very different comparing with those for the corresponding pure CD. But for the composites with 20 % wt. of the CD (*i.e.* below the critical concentration) a considerable change of the WLF parameters is observed indicating, in terms of the free volume theory, that the free volume has increased. For the HPC/poly(AA) or HPC/poly(MAA) composites only the b-relaxation of poly(AA) or poly(MAA), respectively, is visible and it appears at lower temperatures, meaning that HPC modifies the hydrogen bond interactions of the polyacids. The activation energies of the b-relaxations of poly(AA) and poly(MAA) don't practically depend on the composition of the composites. Using the time-temperature superposition procedure, it was possible to estimate the Havriliak-Negami parameters for the b-relaxation of poly(AA) in the HPC/poly(AA) composites and to determinate the distributions of the relaxation time. The dielectric measurements confirm our hypothesis concerning the influence of the intermolecular interactions on the relaxation processes.

At higher temperatures the dielectric response of all the investigated materials is dominated by ionic conductivity, therefore the relaxation processes in the high temperature range was measured by means of the DMA only. The results of the DMA agree well with the dielectric measurements at low temperature range, and additionally they allow to investigate the a-relaxations of the polyacid components. We have measured also the anisotropy of the mechanical properties of the composites. The observed influence of the b-relaxation phenomena on the strength modulus anisotropy can be explained in terms of the intermolecular interactions.

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DETERMINATION OF MOLECULAR NONLINEAR OPTICAL PROPERTIES

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New organic materials with large nonlinear coefficients can be studied by the electric-field-induced second-harmonic (EFISH) generation. This technique allows the determination of molecular second-order polarizabilities by measuring the frequency-doubled light generated in a dilute solution under the influence of a static electric field. The actually measured microscopic quality is $(\gamma + \mu\beta/5kT)$, where γ is the third-order polarizability $\gamma(-2\omega,\omega,\omega,0)$, μ is the permanent dipole moment of the molecule and β is the second-order polarizability. For strongly conjugated organic molecules the purely electronic effect described by $\gamma(-2\omega,\omega,\omega,0)$ can be neglected with regards to the molecular reorientation contribution $\mu\beta/5kT$. The second harmonic (SH) intensities from new organic materials and from a known organic compound COANP (measured in 0.1 - 1 % weight solution with dioxane) were compared with the SH signal from the reference crystal SiO_2.

LOW FREQUENCY DIELECTRIC PROPERTIES OF PHARMACEUTICAL MATERIALS

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The stability of pharmaceuticals, particularly in the freeze-dried state, is dependant upon a number of factors including the degree of hydration, states of water (free, hydration, bound) and general molecular mobility. Dielectric relaxation spectroscopy (DRS) is therefore becoming increasingly important as a research method and, ultimately, is likely to be included in formulation methodologies. Low frequency studies (10^-1 to 10^6 Hz) of microcrystalline cellulose, an important excipient used in tableting, are presented demonstrating the sensitivity of a blocking electrode arrangement in powder samples at low levels of hydration. This particularly concerns a dispersion in the range 10^3 to 10^5 Hz, which we have modelled using the Havriliak-Negami relation, and which would otherwise be dominated by interfacial electrode polarisation.

The physical principles involved in these dispersions are discussed, including the possibility of a charge-hopping mechanism and the effect of particle size and hydration. Possible applications to other nearly-dry pharmaceutical systems will also be mentioned.

HIGH-FREQUENCY DIELECTRIC SPECTROSCOPY OF SOME HIGH PERMITTIVITY MICROWAVE CERAMICS

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Infrared reflectivity and submillimetre transmission spectroscopy have proven recently to be a valuable tool for analysing the value and origin of microwave permittivity and losses in many materials [1,2]. For low microwave loss materials the microwave permittivity is determined basically by polar phonon mode contributions in the 10^{12}-10^{13} Hz range so that the permittivity is dispersionless below ~ 10^{11} Hz. The microwave losses are much more sensitive to defects and consist of two additive parts: intrinsic losses caused by multiphonon absorption (mainly two-phonon difference processes around room temperature) and extrinsic losses due to defects (mostly charged point defects). The intrinsic losses are proportional to frequency, up to ~ 10^{12} Hz, $\varepsilon''(\omega) \propto \omega$, and should rapidly decrease on cooling. The extrinsic losses mostly also obey the proportionality $\varepsilon''_{ext}(\omega) \propto \omega$, but are essentially temperature independent.

In this contribution we summarize our recent results of infrared reflectivity and submillimetre transmission measurements on the following high-permittivity perovskite-like ceramics (ε' values from ~ 40 to ~ 400) : $(La_{2/3})_{1-x}Al_xTiO_3$ (x=0.04, 0.06, 0.1, 0.3, 0.5), $AgTa_{1-x}Nb_xO_3$, (x=0, 0.3, 0.43, 0.5, 0.6, 0.7, 1), $BaLnTi_4O_{12}$ (Ln=La, Pr, Nd), $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $Ba_2Sr_3Nb_4O_{15}$, $BaNd_2Ti_3O_{10}$, $BaSm_2Ti_3O_{10}$, $Ba_xSr_{1-x})(Zr_yTi_{1-y})O_3$ (x=0.27, y=0.25, 0.5, 0.65, 0.8, 0.9, 0.973). The reflectivity was evaluated using a classical or generalized multi-oscillator model to calculate the dielectric function (permittivity and loss spectra). The extrapolation to microwave range enabled us comparison with directly measured microwave dielectric properties. For permittivity values up to about 100 only one-phonon contributions determine the microwave ε' values and permittivity shows no appreciable dispersion below the submillimetre range. For higher permittivity values as a rule an extra sub- or near-millimetre relaxational dispersion appears in the permittivity spectrum which is responsible for higher microwave losses. It appears that such systems have more anharmonic lattices and are close to the ferroelectric instability.

The collaboration with many laboratories which provided us with the high-quality ceramic samples is acknowledged.

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DIELECTRIC SPECTROSCOPY OF CONFINED SMECTIC LIQUID CRYSTAL PHASES

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The behaviour of liquid crystal phases under geometrical restrictions has found a broad interest in contemporary research [1, 2]. A long-standing problem of considerable scientific and technological importance is to improve the understanding of geometry-dynamics correlations in porous materials. We are concerned with the question which properties of the complex random geometry of the porous material have a significant influence on the dynamic properties of the liquid crystal mesophases. We investigate the influence of geometric confinement on the dynamics on a ferroelectric smectic C*. Molecular and collective relaxation processes are studied by means of broadband dielectric spectroscopy in the frequency range from 10^{-2} to 10^{9} Hz. In order to derive general conclusions on the collective dynamics under geometrical restrictions, samples of different pore sizes and geometries have been used [3]. ANOPORE filters provide well defined straight cylindrical channels with a relatively large diameter of 0.2 μm and length of about 60 μm. Cellulose membranes have irregular geometry, a broad distribution of cavity sizes, typically in the submicrometer range, with partially fractal geometry. Porous sol-gel glasses studied here are characterized by very small pores (radii of a few nanometer), irregular distribution of the pore axes but relatively small pore size distributions. Dielectric spectra of DOBAMBC, ZLI, 4237 and CE8 (from *Merck*) have been measured in the adsorbed samples and bulk phases. Several relaxations processes have been obtained in the bulk state. In the isotropic phase we observed two relaxations which are assigned to the rotation around the molecular short axis (the low frequency process) and around the molecular long axis (high frequency process). The high frequency relaxation can be observed through all mesophases. Its frequency does not show any jumps at the phase transitions but only a continuous Arrhenius-like shift towards lower frequencies. In the SmA phase we observe the same molecular processes as in the isotropic phase, the slower one has a frequency shift at the phase transitions. These modes also exist in the SmC* phase. In the bulk sample, an additional Goldstone mode appears in SmC*. From comparison of the observed relaxation processes, we conclude that the molecular processes in all mesogens are uninfluenced by the confinement, even in the nanometer pores a bulk-like relaxation rate is measured. In contrast, the influence of the geometrical restrictions on the collective relaxation processes in the smectic C* phase is dramatic. In the ordered microporous material (pore size 200 nm) the Goldstone mode (GM) is still observed, it is shifted to lower frequencies compared to bulk samples by a factor of about 5. In the non-ordered cellulose membranes and nanoporous glass (7.5 nm) we observe a complete disappearance of the GM process [4]. An explanation for the disappearance of the GM in nanometer pores is straightforward. The limited cavity sizes suppress the free reorientation of the director in the smectic C* material. The confined liquid crystal may still be polar but is no longer ferroelectric. We suggest that for an explanation of the behaviour of cellulose membrane confined liquid crystal, dislocations induced in the smectic layer structure from the irregular cavity walls play the dominating role. The state of disorder induced by the defects prevents the free reorientation of the director and leads to the suppression of the collective dynamic modes.

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THE INFLUENCE OF EXCLUDED VOLUME ON TRANSIENT CURRENTS IN THIN DIELECTRIC LAYERS

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We present some preliminary results of Monte Carlo calculations of classical low-signal isothermal time-of-flight transient currents in thin porous dielectric layers. The calculations have been performed assuming that the layer contains in its bulk a certain number of spherical disjoint pores. The pores are completely inactive in the transport process, which is assumed to go on only in the dielectric matrix thanks to the carriers hopping between localised centres. Such a model may also correspond to a granular material, where the spherical granules have much higher resistivity then the matrix, or may be a rough approximation to a homogenous dielectric with deeply trapped charge carriers which act as spatially extended antitraps.

The Monte Carlo algorithm for calculation of transient current follows the general guidelines described in [1, 2], however, the transport centres of average concentration c were generated at random out of the excluded volumes, so that the centre distribution has a full off-diagonal disorder. The on-diagonal disorder has been introduced by assigning to the centres random energies from a Gaussian distribution of width σ. The transport-inactive volumes (pores) were generated using stochastic geometry methods [3]. The pore distribution is characterised by the following parameters: coverage p of the total layer volume, $0.0 \leq p \leq 1.0$, average radius r_0, and standard deviation σ_r of the Gaussian sphere radii distribution. During the excluded volumes generation the periodic boundary conditions have been applied in all three dimensions. In order to minimise the effects due to a specific spatial distribution of inactive regions, a new distribution of pores was generated for each 20 injected carriers, and the procedure was repeated typically 150 times.

The Monte Carlo calculations have been performed for the following ranges of parameters: $p = 0.0 \div 0.4$, $r_0 = a \div 5a$, $\sigma_r = 0.0 \div 0.5\ r_0$, where a is the average distance between localised states in the conducting matrix (in particular, $a = 0.7$ nm), and $\sigma = 0.0 \div 3.5\ kT$. Other parameters were common for all simulations: reciprocal

Bohr radius of the hopping centres $\alpha = 2.5/r_0$, temperature $T = 400$K, external electric field $E = 1.0 \cdot 10^8$ V/m, layer thickness $L = 70\ a$, frequency factor $\nu = 10^{13}$ Hz.

The results may be summarised as follows: 1. increasing p for constant r_0 and σ_r results in an increase of the effective time-of-flight; 2. increasing r_0 for constant p shortens the effective time-of-flight; 3. in both previous cases the current slope in the post-time-of-flight region systematically decreases; 4. the increase of σ and σ_r makes the previous effects (1-3) weaker. As an illustration, in Figure 1 we show the r_0 - dependence of the effective time-of-flight and the final current slope in the log-log scale.

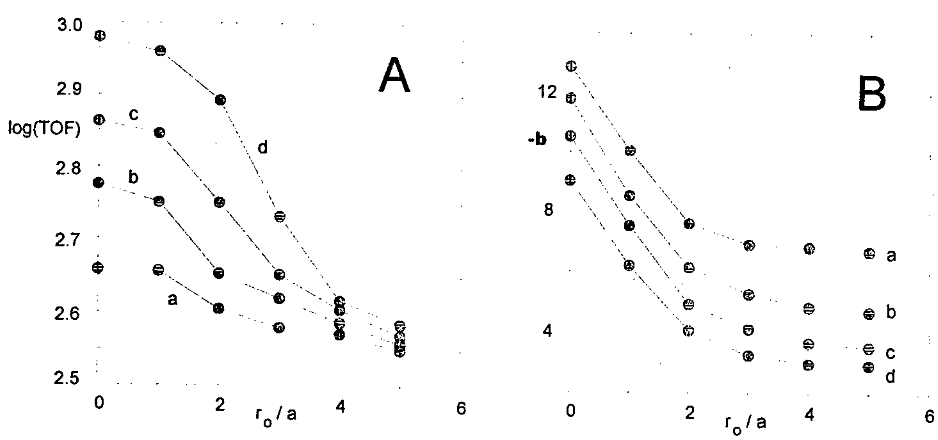

Figure 1. The dependence of the effective time-of-flight (A), and the final current slope (B) on the pore radius r_0. Curves a: $p = 0.1$; curves b: $p = 0.2$; curves c: $p = 0.3$; curves d: $p = 0.4$. Hopping centre concentration in the matrix $c = a^{-3}$, time in Figure A is normalised to the average carrier jump time in a cubic lattice with six nearest neighbours of corresponding density. $\sigma = 0$, $\sigma_r = 0$.

The opportunity to perform our MC simulations at the TASK Computer Centre in Gdańsk is kindly acknowledged.

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DIELECTRIC PROPERTIES OF FERROELECTRIC-METAL MICROCOMPOSITES

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The composite systems are compound from the macroscopic grains of constituent materials, but these nonhomogeneities are small in comparison with measuring probes such as electromagnetic or ultrasound waves, that examine the effective medium properties. Finite size effects including depolarization effects and intergrain interactions (like dipole-dipole interactions and interactions of higher multipoles, or direct intergrain mechanical interactions) may lead to new effective properties of the resulting medium. Dielectric and mechanical properties of such materials are not formed by a simple addition of properties of individual components considering both their static (e.g. ferroelectric transition) and dynamic (e.g. soft mode) properties.

We study the dielectric response in two-phase composites of ferroelectric material and metal within the quasistatic approximation [1,2,3]. Using the effective medium approach and the Bergman representation the dielectric function is represented as a distribution of polar modes corresponding to the geometrical modes of the ferroelectric material (the lowest frequency corresponds to the transverse optical soft mode) and the geometrical modes of the metal. The temperature and the concentration dependences of the dielectric spectrum are investigated. The composite is conductive in the case of percolated metal. Below the percolation threshold of the metal the composite undergoes the ferroelectric phase transition at the same temperature T_C as the bulk ferroelectric material, but with the higher Curie constant. The theoretical description will be applied to some real materials.

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DIELECTRICAL PROPERTIES OF THIN MOLECULAR FILM-STRUCTURES

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As quantum low-dimensional structures are of current interest [1,2], we tried to formulate a microscopic theory of dielectrical properties of thin molecular films, i.e. quasi-2D systems bounded by two surfaces parallel to *XY* planes [3,4]. Harmonic exciton states [5] were calculated using the method of two-time, retarded, temperature dependent Green's functions [6]. It has been shown that two types of excitations can occur: bulk and surface exciton states.

Analysis of the optical properties (refraction and absorption coefficients) of these crystalline systems for low exciton concentration shows that the absorption and the refraction phenomena are present for all wavelengths and strongly depend on boundary parameters of the film. Conditions for the appearance of localized exciton states are especially interesting and have been analysed in this work.

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POLARIZABILITY ANISOTROPY OF CB N MOLECULES

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The main feature of liquid crystals are their anisotropy. The anisotropy of dielectric permittivity, viscosity and berefringence. Anisotropy of some phenomenon means that same two vectors, which describe this phenomenon, are not parallel themselves. In the dielectric properties the induce vector D_i may be calculated from expression $D_i = \varepsilon_{ij} E_j$, where ε_{ij} is a tensor of dielectric permittivity of liquid crystal sample and E_j is electric field intensity. For a berefringence we have relationship between induced dipole moment and polarizability tensor α_{ij} multiplied by electric field intensity E_j. If we want to investigate of liquid crystal physical properties we must have a information about liquid crystal molelecules. Recently we tern our attention on the three quantities, which are connected directly with the liquid crystal molecule properties. To these quantities belong the trace α_s of polarizability tensor, its components $\alpha_{\|}$ and $\alpha_{\perp}$ and polarizability anisotropy $(\alpha_{\|}-\alpha_{\perp})$. Trace of polarizability tensor is not depended on the main coordinate systems and may characterise the conformation change of molecule. The polarizability tensor components $\alpha_{\|}$ and $\alpha_{\perp}$ have the same features but their quantities are changed when the coordinate system is changed too. Very important physical quantity is a polarizability anisotropy $(\alpha_{\|}-\alpha_{\perp})$, because it is independent with temperature for nematic or smectic and isotropic liquid states. We can say the $(\alpha_{\|}-\alpha_{\perp})$ is a visiting cart of liquid crystal molecule. In this work the mentioned above quantity was investigated for homologous CB n for n equal 5 to 9. For calculation we use the equations, which was proved by us and printed in the literature [1-6].

$$(\alpha_{\|}-\alpha_{\perp}) = (M/N)\,[(n_e + n_o)/k_A d]$$

$$\alpha_{\|} = (M/N)\,[(n^2 - 1)/d + 2(n_e + n_o)/3\,k_A d]$$

$$\alpha_{\perp} = (M/N)\,[(n^2 - 1)/d - (n_e + n_o)/3\,k_A d]$$

By the investigation of these quantities we want to test how the change of molecule about CH_2 group influence on the its properties. In this aim we take the homologous CB n, which molecule core is constant. Besides we calculated the order parameter $S = 1/2(3\cos^2\theta - 1)$ of these liquid crystals.

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HOPPING TRANSPORT IN A DISORDERED LATTICE SIMULATION OF DARK DISCHARGE

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The understanding of the diffusion process of particles in a disordered medium (e.g. for charge carrier transport in amorphous substances) is a challenging physical problem. In particular the description of correlations which arise due to the exclusion of multiple occupations of sites for higher charge carrier concentration requires careful modelling. A model was put forward by Liemant and Brehmer [1] for the microscopic description of the charge transport based on the stochastic theory of exclusion processes and aimed at the hopping transport of charge carriers via localised states in a disordered medium. The large time-space scale limit of the theory leads to a description of charge transport by non-linear differential equations, with transport coefficients (diffusivity and conductivity) which vary with the average occupation of the localised states. In the microscopic model the dynamics is controlled by the hopping (jump) probability from an initial state at x with energy E to another state at y with energy Q:

$$w(x,E;y,Q)=\gamma\ \exp\left(-\frac{Q-E+e(\varphi(y)-\varphi(x))}{2kT}\right). \qquad (1)$$

Taking a microscopic average the hopping range covers, from a macroscopic point of view, a region which contains many localised states. Due to the finite hopping range the charge carrier can only influence a small region in its immediate neighbourhood, reaching local thermodynamic equilibrium on a microscopic time scale. Each small region within the sample is characterised by a local value of the chemical potential ζ. Using detailed balance a macroscopic charge transport equation is obtained as:

$$\frac{\partial\rho}{\partial t}=div\left(\sigma(\zeta)grad(e^{-1}\zeta+\varphi)\right).$$

Here ρ(x,t) is the space charge density, φ the electric potential and e the charge of the charge carrier. Using (1) with a distribution g(q) of energy states the conductivity is obtained as

$$\sigma(\zeta)=\kappa\left(\int_{-\infty}^{\infty}\frac{\exp((\zeta-q)/2kT)}{1+\exp((\zeta-q)/kT)}g(q)dq\right)^2$$

and the diffusivity as

$$D(\zeta)=\frac{\kappa kTN}{e}\frac{\sigma(\zeta)}{\int_{-\infty}^{\infty}\frac{\exp((\zeta-q)/kT)}{(1+\exp((\zeta-q)/kT))^2}g(q)dq}.$$

The Poisson's equation $div(\varepsilon\, grad\,\varphi)=-\rho$ completes the set of equations needed for a macroscopic model. A solution may be obtained numerically with the boundary and initially conditions being determined by the experimental configuration.

For simulation of dark discharge of a surface charged electret we consider a thin film of thickness L. One side is coated by metal film, which constitutes an electrode. This electrode is earthed while onto the other side located at x=0 a charge ρ_s is deposited. At t=0 no charge carriers are present in the bulk of the material. Thus the initial and boundary conditions take the form:

$$j(0,t)=-\frac{\partial}{\partial t}\rho_s(t),\ \varepsilon\frac{\partial}{\partial x}\phi(x,t)\Big|_{x=0}=-\rho_s(t),\ \rho_s(t)\Big|_{t=0}=\rho_s,\ \rho(x,0)=0$$

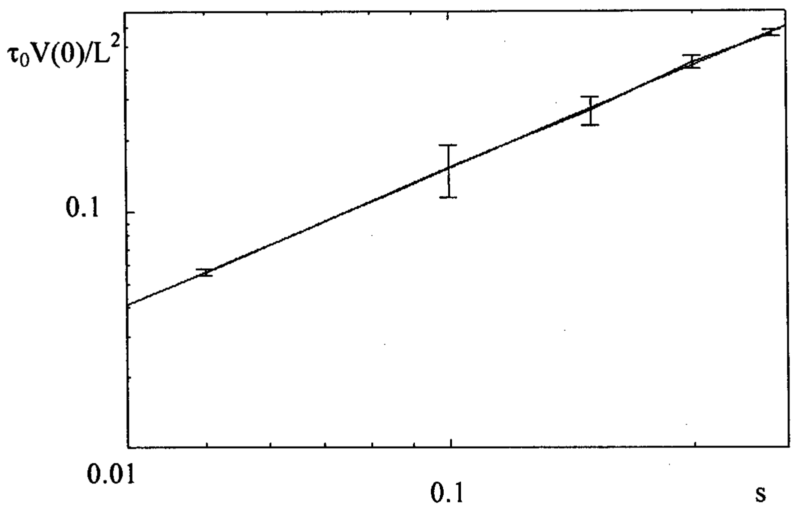
$$\rho(0,t)=eN \text{ and } \rho(L,t)=0.$$

A simulation of the charge transport process yields the space charge evolution ρ(x,t) and the surface potential kinetics $V(t)$. The logarithmic derivative $d\log V(t)/dt$ is found to decay linearly up to $t=\tau_0$ where τ_0 corresponds to the transit time. Thereafter a constant level is reached which is related to the maximum conductivity.

In order to establish the influence of a distribution of energy levels a model is calculated with a Gaussian distribution of energy levels characterised by a standard deviation s. Simulations using L=20 - 100 μm, $V(0)=200-5000$ V and $s=0.05, 0.1, 0.15, 0.2, 0.25$ eV indicate that

$$\tau_0\sim V(0)^{-1},\ \tau_0\sim L^2 \text{ and } \tau_0\frac{V(0)}{L^2}\sim s^{1.44}.$$

Fig. 1: $\tau_0\frac{V(0)}{L^2}$ as function of standard deviation s



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INFLUENCE OF MOLECULAR WEIGHT IN THE THERMALLY STIMULATED CURRENTS SPECTRUM OF A SIDE-CHAIN LIQUID CRYSTALLYNE POLYMER

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Liquid-crystal polymers (LCPs) combine the material properties of solids with the flow properties of liquids. These systems do not show a single transition from solid to liquid, but they pass through one or more mesophases (smetic, cholesteric and nematic phases) before they are transformed into the isotropic liquid. Of course, the formation of the different mesophases types depends on the molecular interactions which are in competition with thermally activated translational and rotational motions [1].

Dielectric measurements are a powerful tool to study the dynamics in liquid-crystal polymers [2]. Investigations of dielectric properties can give information about the distribution of relaxation times associated with reorientation processes of the molecular dipole moments. If a strong dipole is situated in a special position of a molecule, its moment can be used as a detector for the molecular reorientation of the whole mesogenic group. For example, in the liquid crystalline poly({3- [4- (4 – cyanophenyl) phenoxy] propyloxycarbonyl} ethylene) the strong CN-dipole is connected with biphenyl in the side group.

The technique of thermally stimulated discharge currents (t.s.d.c.) is a suitable technique to study the dipolar relaxation mechanisms in polymers [3, 4] and it shows a good capacity for resolving complex relaxation spectra as a function of temperature [5]. This high resolution power of the t.s.d.c. technique is a consequence of its low equivalent frequency [6]. Our objective is to get a deeper knowledge on the relation between structure and relaxation processes. In this context, we use this technique for studying the influence of the molecular weight on the different transitions present in the poly({3- [4- (4 – cyanophenyl) phenoxy] propyloxycarbonyl} ethylene). We analyse the effect of this structural factor in the kinetics of the glass transition and other relaxation processes which can be observed above and below Tg.

The physical aging at temperatures below the glass transition temperature will be studied by t.s.d.c., and the effect of aging on the compensation effect [7,8] will be discussed.

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ELECTROOPTICAL INVESTIGATION OF NEMATIC LIQUID CRYSTALS

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The nematic liquid crystal ZLI-1800-000 with positive dielectric anisotropy $\Delta\varepsilon > 0$, product from "Merck" - Germany, has been investigated with method of electric birefringence and measurements of dielectric constants.

The change of the light intensity is investigated when is applying alternating electric field on a liquid crystal sample with different thickness d = 25; 30; 35; 40 and 50 μm. Measurements has been taken in the nematic phase of liquid crystal in temperature range from 30°C to 60°C.

From these measurements are obtained the optical contrast K of light transmitted in the liquid crystal and ' relaxation time τ_{fall}. Also, for given temperature and frequency of the applied field, the threshold voltage is·determined.

Determination of dielectric perxnittivities $\varepsilon_{\perp}$, $\varepsilon_{||}$ and dielectric losses of this saxnple is achieved by the use of Hewlett-Packard's Impedance Analyzer 4192A. Measurements are realized for different temperatures in frequency range from 5Hz = 10MHz. From dielectric measurement are obtained elastic constants K_{11} and K_{33}, clearing point, change of dielectric anisotropy for different frequencies and graphical presentation in ε', ε" diagrams (so called Coul-Coul diagrams).

INVESTIGATION OF THE SUB–TG RELAXATION PROCESSES IN POLYURETHANE SYSTEMS BY DIELECTRIC AND MECHANICAL SPECTROSCOPIES

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Sub–Tg relaxation processes in polyurethane systems, based on (poly-propylene glycol) triol and hexamethylene diisocyanate (HMDI) at different reaction extents, are investigated by several techniques Dielectric Relaxation Spectroscopy (DRS), Rheology and Ultrasonics. The purpose of this study is to compare the relaxation processes probed by these techniques in terms of distribution of relaxation times, activation energies and their evolution with the degree of connectivity. Quenched samples corresponding to different reaction extents are obtained after complete reaction by varying the initial stoichiometric ratio defined as the ratio of the concentration of isocyanate groups to hydroxyl groups. Three triols of different molar masses (260,700 and 6000 g/mole) are used in order to apprehend the influence of the macromolecular chain size on systems dynamics.

DIPOL RELAXATION PROCESSES IN ELECTRON-IRRADIATED AMORPHOUS CHALCOGENIDE SYSTEMS

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The microstructural processes of dipol relaxation associated with so-called diamagnetic coordination defects are studied in electron-irradiated amorphous chalcogenides based on arsenic trisulphide using optical spectroscopy method as well as far IR Fourier-spectroscopy technique in the range of main vibrational bands.

Investigated samples of amorphous chalcogenide systems were prepared by traditional method of direct melting of chemically pure initial constituens in evacuated quarz ampoules. The amorphous trisulphide arsenic samples were chosen as model objects in our experiments.

It is shown that high-energetic electron irradiation (E=2.8 MeV) with fluences more than 10^{15} cm^{-2} leads to the formation in the structural network of investigated samples a specific defects revealed themselves as dipol atomic pairs contained under- (negative electrical charge) and over-coordinated (positive electrical charge) atoms. These dipols are oriented along direction of electron flow propagation and subsequently produced an electron-stimulated anisotropy of the samples.

Time- and temperature-related dependences of the observed anisotropy effect decreasing connected with relaxation processes of coordination dipols reorientation and annihilation are discussed detailly at the basis of obtained experimental results. It is obtained that the magnitude of electron-induced anisotropy effect depends on chemical composition of amorphous samples.

Observed processes are described mathematically using topological approach to the coordination defects formation processes in amorphous chalcogenide semiconductors. All statistically possible topological variants of defects are taken into account for amorphous chalcogenide semiconductors of concrete chemical composition. The concentration of the coordination defects are calculated in the framework of the theory of elastic displacements of atoms due to bombardment electrons with high energy.

The practical aspects of investigated vitreous semiconductors application in the optical dosimertic systems are discussed.

INVESTIGATIONS OF DYNAMICS OF N-P-(ETHOXYBENZYLIDENE) P'-PROPYLANILINE (EBPA) MOLECULES IN PLASTIC PHASES

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Studies of dynamics of the EBPA have been performed using the dielectric relaxation method in the frequency range from $10^0 - 10^7$ Hz. Measurements of ε' (ν) and $\varepsilon''(\nu)$ cover the temperature range from 200K to 360K. Heating and cooling rates between 0.5 - 20°/min have been used.

In the earlier DSC and polarizing microscopy studies of EBPA the following phases were detected: isotropic liquid , nematic liquid crystal, and two crystalline phases, the metastable K_1 and the stable K_2 [1]. Dielectric studies confirmed this results. The frequency range applied was particularly suitable for observation of the reorientational motions in plastic crystalline phases. It is interesting that both K_1 and K_2 phases occurred to be the mobile ones. Analysis of the dielectric absorption shows that the relaxation observed in each phase is complex. It has been described by surn of two Cole-Cole formulas which gives evidence of two molecular motians in both plastic crystalline phases. For one of this processes the phase transition from the metastable phase K_1 to the stable phase K_2 is accompanied by the drop of [3 parameter describing the broadening of the absorption curve and by significant change ofthe dielectric increment Oc.

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DIELECTRTC PROPERTIES OF MIXTURES OF CHITOSAN AND DICLOFENAC SODIUM

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Chitosan shows very interesting biological, chemical and physical properties which enables its various practical applications [1,2]. For instance, chitosan rnay be used in pharmaceutical, cosmetic and food industry, biotechnology etc. The biological and chemical properties of chitosan may also depend on its physical structure. It has been shown that broadband dielectric measurements may enable to detect the recrystallization phenomena of solid organic materials [3]. The basic aim of the presented research was to monitor the ageing phenomena of chitosan and its mixture with diclofenac sodium.

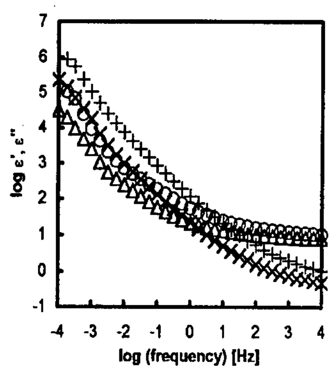

Fig.1.Comparison of the dielectric response of chitosan/diclofenac sodium (DS) mixture. The content of DS was about 15%. C: o virgin sample, Δ sample annealed at 40°C for 5 h. G/ω: + virgin sample, x Δ sample annealed at 40°C for 5 h.

Dielectric properties of microcrystalline chitosan (MCCh, from Institute of Chemical Fibres, Lodz, Poland), dielofenae sodium salt (DNa, Sigma Chemical Co.) and their mixtures have been studied. Microcrystalline chitosan in the fonn of water gel was characterised by 3.4 % of the polymer content, viscosimetric molecular weight Mv = 202 kDa, degree of deacetylation (DD) equal to 85.7%. The samples were prepared in form of compressed disks. Firstly, a microcrystalline chitosan hydrogel and its mixture with drug (the weight relation MCCh:DNa = 3:1) was spread on a Teflon plate and the water was evaporated at room temperature. After the evaporation of water a xerogel film was obtained and then crumbled in order to get it powdered. Next it was mechanically blended and compressed. The samples were pellets obtained by compression of the powdered materials. The weight of the pellets was about 0.1 g, their thickness was about 0.5 mm. The pellets were supplied with metal (gold or aluminium) electrodes of the diameter of 9 mm. The measurements were carried out in the frequency range 1 mHz ÷10 kHz. The samples were aged at the temperatures up to 80°C for about

5 hours. 'The ageing phenomena in the temperature range used have been detected in all the investigated systems. The ageing phenomena may be either due to partial crystallisation of the investigated systems or due to additional chemical bonding of the molecules which makes the molecular movement of some polar groups more difficult. In order to characterise the detected ageing phenomena the additional investigations of infrared (IR) absorption of the systems has been carried out.

The IR absorption studies have enabled to find a more precise interpretation of the obtained results. For the purpose the IR investigations the samples were prepared in the form of compressed pellets 0.5 mm thick consisting of KBr and the investigated material (1 mg of the investigated material +300 mg KBr) or in the form of thin film 5 mm thick. The film consisted of MCCh and its mixtures with the drug (MCCh:DNa=3:1, 2:1, 1:1). The samples were kept for 5 h at the temperatures: 20 C, 40 C, 60 C, 80 C, 100 C, 1 15°C, 130°C. Then IR spectra were analysed using a Mattson spectrophotometer after cooling down to the room temperature. Some insignificant decrease of the intensity of characteristic bands of chitosan and the drug has been detected for the ageing temperatures in the range 20°C =60°C. Starting from the temperature 80°C a remarkable change of the IR absorption has been detected. In this situation it may be suggested that the detected change of the dielectric response is due to change of crystallinity of the samples. Further RTG and DTA studies are planned to confirm the above suggestion.

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CONFORMATIONAL DYNAMIC OF FIBRINOGEN BY DIELECTRIC SPECTROSCOPY

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The conformational stability of a protein is determined by intermolecular factors and solvent interactions (hydration). Like other polymers, proteins can be characterized by their chain conformation. All proteins adopt specific (native) conformation under physiological conditions. Hydration plays a major role in the maintenance of the native state. The physical properties of water, too, are sensitive to the same factors that influence protein stability, so that some connection is likely.

It is now accepted that protein hydration interactions are of crucial importance in the maintenance of higher order structures and in rendering proteins useful as technological macromolecules. However, there is as yet little understanding about the details of such interactions and their role in determining the functional attributes of proteins.

Fibrinogen is the main protein of blood clot system consisting of the three pairs of non-identical polypeptide chains. External factors such as temperature, pH, ionic strength influences fibrinogen conformation and function as coagulation factor. High- and low-temperature transitions in fibrinogen are well known [1,2]. But all of them have been obtained under specific conditions. In order to trace the conformational dynamic of fibrinogen molecule under physiological conditions we have studied the influence of the temperature (in range 4-50°C) on the 0.15M NaCI (pH 7.2) fibrinogen solution by using microwave-dielectrometry method.We have used the microwave-dielectrometer of resonant type [3] to study dielectric properties of the fibrinogen solution at the frequency equal 9.2 HHz, in the range of dispersion of the free water molecules.

The temperature dependences of the real ε' and imaginary ε'' parts of complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ of the fibrinogen solution have been measured. It has been shown that in the 0.15M NaCI solution increasing of the s' and decreasing of the ε'' are typical with temperature inereasing. The temperature dependences of the dielectric parameters of fibrinogen solution have a number of peculiarities at 8-10°C, 20-22°C and 35°C. At these temperatures the deviation from monotonousity of the temperature dependences of the real and imaginary parts of complex permittivity of the fibrinogen solution has taken place. Such a deviation has not been observed in the case of pure solvent.

At increase of temperature ε' is in the beginning monotonously increased, that is caused by reduction of durability of hydrogen bonds between water molecules in result of their thermal traffic. Further, at temperatures 8-10°C direction of temperature dependence of ε' in party of dawnturn is sharply changed. Hence it results in consolidation of hydrogen bonds of water in solution (which is believed to be connected to the conformational transition in the fibrinogen molecule at given temperatures). After it ε' again monotonously grows with increase of temperature up to 20-22°C, where there is the recession. The similar recession occurs at temperatures above 35°C.

These facts indicate the change of the free water state in the fibrinogen-water system at temperatures 8-10°C, 20-22°C and 35°C. Probably at these temperatures there is the conformational change of a fibrinogen molecule.

Thus besides known temperature transitions I and II, conformational change at 20-22°C has taken place in fibrinogen.

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LOW FREQUENCY ELECTRICAL PROPERTIES OF NON-CROSSLINKED EPOXIDE MATERIALS.

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Time domain dielectric spectroscopy technique has been used for evaluation of low frequency electrical properties of epoxide materials. The following materials were used for measurements : Epidian-3, Epidian-5, Epidian-6 and Epon 828. They were tested in noncrossliked state. Epidian-3 was tested below and above glass transition temperature T_g, while Epidian-5, Epidian-6, and Epon 828 were tested above their T_g. Plane -parallel electrodes made of ITO (indium-tin oxide) or Cu were used. In majority of cases the thickness of the sample was equal to 0.2mm. Time domain investigations enable to evaluate the following phenomena:
-charge polarization phenomena,
-sample electrical conduction due to mobile ions,
-sample conduction phenomena due to localized carriers,
-sample conduction phenomena due to electrode emission (electrode currents).
All these phenomena can be analysed in terms of known models of charge transport, diffusion, recombination, dissociation of neutral species and electrode emission. As general, the data are nonlinear in respect to voltage change. It is true in case of electrode currents, as shown in Fig.1 and 2.

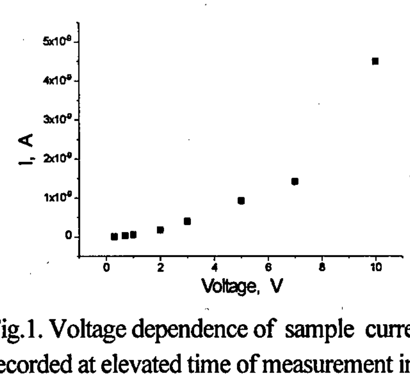

Fig.1. Voltage dependence of sample current recorded at elevated time of measurement in Epidian-3 below glass transition temperature. Sample thickness 0.2mm.

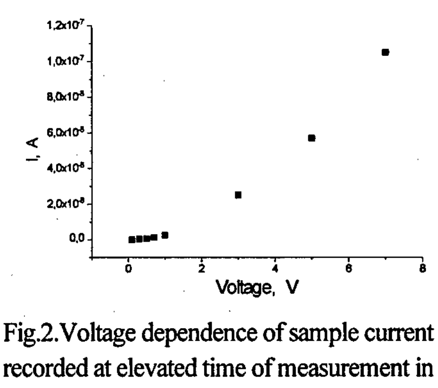

Fig.2. Voltage dependence of sample current recorded at elevated time of measurement in Epidian-3 above glass transition temperature. Sample thickness 0.2mm.

For quasi-linear current vs voltage relation it was possible to proceede the comparison with Frequency Domain data by means of Fourier transformation of measurement results.

In similar manner current vs temperature dependence was evaluated. In most of cases Arrhenius-like dependence was obeyed. It is assumed, that certain time polarisation process is terminated. The indication of this moment is negligible value of depolarisation current. Electrode current evaluated by means of subtraction of discharging file from charging one is not quasi-independent of the time of measurements as it is encountered in liquid crystals.

The dependence of the electrode current of the time of measurement may take different forms. For example a plot for Epidian3 recorded at 298 K is shown in Fig.3a. One may suggest the overlap several exponential functions.

However the slopes calculated from the plot are voltage dependent, increasing with voltage increase.

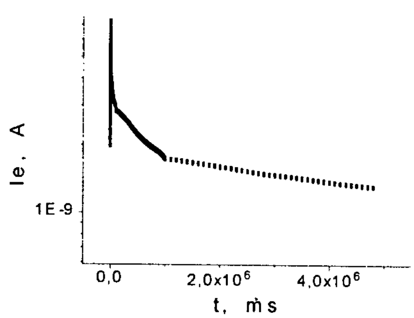

Fig.3a. Time dependence of electrode current (in log-lin scale) recorded for Epidian-3 below glass transition temperature. Voltage applied U=7V, sample thickness 0.2mm.

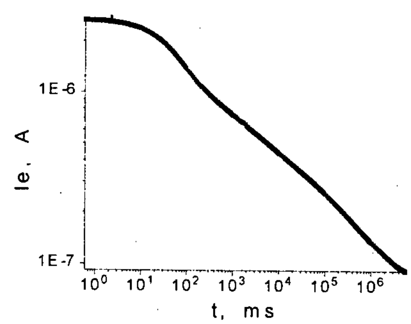

Fig.3b. Time dependence of electrode current (in log-log scale) recorded for Epidian-3 above glass transition temperature. Voltage applied U=7V Sample thickness 0.2mm.

On other hand decay observed above T_g, (at 333K), as displayed in Fig.3b, is fractal in respect to time, means $I_{el} \approx t^{-n}$, where n value also depends on voltage.

These findings may suggest, at least, diffusion processes to be operational in material space charge layer.

INVESTIGATION AND DIELECTRIC MONITORING OF CROSSLINKING REACTION IN THERMOSETS AND ELASTOMERS WITH MICROWAVE METHODS

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In the case, when some problems complicate the crosslinking reaction monitoring with low frequency dielectric measurements (high conductivity of some materials or products of the reaction, additional low frequency relaxation processes, etc.), mask the useful information and reduce the sensitivity, we propose to use the microwave (MW) methods. To prove the efficiency of the MW methods we investigated 3 types of thermosets during the curing process (urea-formaldehyde, melamine-phenolic and phenolic resins) and 3 sorts of elastomers during vulcanization (carbon black filled rubbers with different carbon concentration and activity).

Well pronounced maximums of the MW dielectric parameters were observed for all investigated thermosets, corresponding to increasing and decreasing of the molecules mobility during softening and curing. Low values of the MW dielectric permittivity and losses prove that MW dielectric parameters are defined by the fundamental polarization mechanism, caused by the dynamics and kinetics of the polymer molecules, and include no contributions from conductivity and low frequency relaxation processes. Vulcanization of elastomers also resulted in the changes of MW dielectric parameters, depending on carbon black concentration and activity and defined by the polarization mechanisms, caused by the rubber-carbon interface phenomena and by the dynamics of rubber molecules. So, MW methods are sensitive to the crosslinking reactions in thermosets and elastomers, reflect the changes in the polymer network even in the case of high enough conductivity.

We modified the open-ended coaxial line resonator method and adapted it by the construction of high-temperature, high-pressure stable coaxial sensor for on-line curing monitoring of moulding compounds during pressing and injection moulding. This method has successfully tested on the thermosets under conditions close to the industrial technological process (closed volume, pressure, heating) and on the elastomers during vulcanization. We propose this method for technological testing and on-line monitoring of crosslinking reaction.

SIMULTANEOUS STUDY OF TOPOGRAPHY AND LOCAL ELECTRICAL PROPERTIES OF DIELECTRICS: SCANNING CAPACITANCE, CONDUCTIVITY AND SURFACE CHARGE MICROSCOPY

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Two new techniques, extending the features of Scanning Force Microscopy (SFM) and able to visualize the local electrical properties' distribution (SFM+E), are proposed as an analytical tool for studying of dielectric materials of different kinds: polymers, composites, ceramics, crystals, etc. A commercial SFM with contact and non-contact options is modified and its two external ADC inputs are used for the investigation and imaging of the local complex conductivity and the surface charge distribution. The possibilities of SFM+E methods are illustrated by the experiments on different heterogeneous systems, whose electrical properties cover a wide range of conductivity and dielectric parameters: 1) polyphase ceramics: $BaTi_4O_9$ with dielectric and conductive phases, due to the partially reduced titanium valence state; ferroelectric $BaTiO_3$-based with coexistence of crystalline and amorphous phases; posistor semiconductive, based on $BaTiO_3$; 2) heterogeneous films: conductive organic; additive containing polymeric; structurally charged electret polymeric; dewetted polymer blend; ferro- piezoelectric PZT; 3) carbon fibers - polymer composite.

All the materials are characterized by the heterogeneous distribution of surface charge or of complex conductivity. The phase heterogeneity of the ceramics, films and composites is clearly demonstrated by the local electrical properties distribution. There is a correlation between topographical and electrical heterogeneity, but not the coincidence. Volume and surface distribution of the electrical parameters (so, phase structure too) are more fine than grain structure. Visualization of the electrical heterogeneity gives additional information about composition, phase-, crystallite-, grain- or domain- structure of the materials to the conventional **SFM** topography images. Nano-scale electrical (phase) heterogeneity (~10 nm) can be visualized. The simultaneous visualization of the surface topography (grain structure), polyphase structure and electrical heterogeneity can be considered as a new effective method for microanalysis of heterogeneous, polyphase, polydomain, disordered materials (especially electro-active ones: polar, ferro-, piezo-), as bulk as film or composite ones.

DIELECTRIC RELAXATION OF THIN FILMS BASED ON PMMA AND POLYIMIDE

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For the first time using the method of low-frequency dielectric dispersion new polymeric systems based on PMMA and fluoride cardo polyimide (PI) [1] were considered.

The estimation of their dielectric characteristics, such as the loss tangent and complex dielectric permittivity, was performed in the frequency range 20Hz20kHz and temperature region 230-330 K.

Comparison was made between the complex permittivity plots for PMMA, PI and their copolymers of composition 10/90 and 25/75 accordingly and it was showed, that the leading role in relaxation processes is that of PI even at its 10% - content in the copolymer. From the experimental data the satisfaction of the universal law of dielectric response [2] follows, and considering the values of power parameters of this law it can be said that there occurs rather wide relaxation time spectrum and the diffusive mechanism of free ion transport prevails.

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DIELECTRIC BEHAVIOR OF BiSrCaCuU SAMPLE

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Looking for a new insight on the high Te materials the dielectric behavior of a sample of the cuprate BiSrCaCu4 in the frequency range between 20 Hz and 1 SO MHz has been observed. The sample has been prepared by the solid state reaction followed by a sintering procedure at 890 °C starting from oxides and carbonates in the powder state . The real and imaginary components of the complex permittivity have been determined from measurements performed using a plane electrodes cell connected to an impedance analyzer bridge. The dielectric behavior, which. can be described by an asymmetric are, has been observed in the temperature range varying between 77 and 293 K.

DIELECTRIC BEHAVIOR OF LEMON JUICE AND MODEL SYSTEMS

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In order ta determine the influence of each natural clarified lemon juice components in the dielectric behavior between 20 .Hz and 150 MHz, model systems of the lemon juice composed by mineral water, dextrose and citric acid at different concentrations have been prepared and its real and irnaginary permittivity components have; been measured at the room temperature. The measurements were performed using a plane electrodes cell af varying space between electrodes in order to minimize the effect of electrode polarization. In order to compare, also the dielectric behavior of the natural clarified lemon juice at 60 Brix has been observed.

Looking for an independent evaluation of the electrode influence the permittivity measurements were also made using a alectrodeless cell in the same frequency range.

INVESTIGATION OF OPTICAL SWITCHING OF AZOTHIOLS AND AZO-CONTAINING AMPHIPHILES WITH DIELECTRIC SPECTROSCOPY

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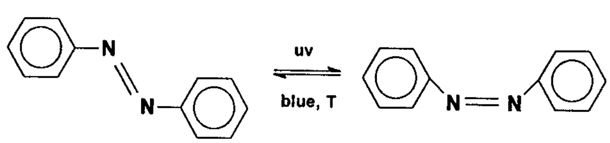
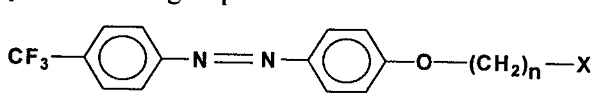
Azobenzene groups of chemical compounds are known for their cis-trans isomerism accessible under irradiation with blue and ultraviolet light, respectively. The trans-isomer with a lower energy level changes to cis-isomer with a higher energy level when irradiated with 360 nm light and switches back under 450 nm radiation or under thermal treatment.



This so-called optical switching is widely examined in literature with a lot of very different methods but there are only a few contributions dealing with dielectric spectroscopy. This method allows in a unique manner statements about dipole movements.

We present results of dielectric spectroscopy in the frequency range from 10^{-2} to 10^{5} Hz on a set of azothiols and azo-containing amphiphiles with strong dipole moment due to a CF_3-group as terminal group.



substances:

Especially we studied the influence of various molecular environments on the dielectric relaxation process of the azo-dipoles as well as the differences between ordered and non-ordered films.

We compare different types of thin and ultra-thin films: Langmuir-Blodgett films (X = COOH), spin-coating films (azothiols dispersed in PMMA matrix) and self-assembled monolayers (SAMs, X = SH); ITO and gold served as substrates.

FAR-INFRARED SPECTROSCOPY OF THE PHASE TRANSITIONS IN HEXAGONAL BARIUM TITANATE

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Hexagonal $BaTiO_3$ undergoes on cooling two structural phase transitions, at 222 K (from the space group D_{6h}^4 to D_2^5) and at 74 K (to ferroelectric phase C_2^2). Far Infrared (FIR) reflectivity spectra of E_{1u}(a) and A_{2u}(c) symmetries show distinct changes with temperature. Temperature changes of the sta.tic dielectric permittivity can be explained by the temperature dependence of the A_{2u} polar soft mode, which was observed in our FIR spectra and also in already published hyper-Raman spectra. The A_{2u} polar soft mode influences the phase transitions together with the E_{2u} silent soft phonon, which induces at least the phase transition at 222 K.

DIELECTRIC RELAXATION IN A SYSTEM WITH THE REENTRANT NEMATIC PHASE

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The phase transition between a one dimensional solid-like smectic A and the three dimensional liquid-like nematic is one of the most important transitions in the physics of liquid crystals. The interest in this transition is enhanced by a variety of smectic A phases for which the parameters describing a structure of layers can be correlated with the molecular structure and the molecular interactions. A relatively small modification of the molecular properties may lead to a considerable change in the stability of the mesophase, and in some cases it may even cause a reversal of the natural phase sequence, for example the nematic phase can appear at a temperature lower than that of the stable smectic phase. Numerous experimental and theoretical papers were devoted to studies of the reentrant nematic phase, which was discovered by Cladis in 1975 [1]. This phase has been observed in mixtures [1,2] as well as in single compounds at high [3] and atmospheric [4] pressure. At presents many compounds and mixtures are known in which a reentrant nematic phase is observed [5,6].

The mixture of 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB) and 4-*n*-hexyloxy-4'-cyanobiphenyl (6OCB) is a classic system in which the stable nematic reentrant phase is observed. Much precise and reliable data concerning this system have been reported in literature [7,8].

Here, we present the results of the dielectric relaxation studies for several compositions of 8OCB/6OCB mixtures in the isotropic, nematic, smectic A and reentrant nematic phases. The measurements were carried out in the frequency range: 100 kHz ÷ 100 MHz. The dielectric strength and the relaxation time corresponding to the molecular rotation around the short axis have been discussed in terms of the dipolar antiparallel pairing leading to the reentrant nematic phenomenon [9].

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PHYSICAL AGING ON META-TOLUIDINE STUDIED BY THERMALLY STIMULATED DEPOLARISATION CURRENTS

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The Thermally Stimulated Depolarisation Currents (*t.s.d.c.*) technique has been used to characterise the dipolar relaxation mechanisms associated with the glass transition in the fragile glass former *m*-toluidine.

The experiments were carried out in the temperature range between –110 şC and -70 şC, after supercooling the liquid from room temperature down to –100 şC, with a cooling rate of 4 şC/min. This thermal treatment prevents the crystallisation processes and gives rise to a non-equilibrium glassy state with a calorimetric glass transition temperature $T_g > -87$ şC [1].

The glass transition peak of *m*-toluidine was studied in detail by the usual technique of Thermal Cleaning (TC). The TC components of the glass transition relaxation showed activation enthalpies which strongly deviate from the zero entropy prediction. This deviation is at the origin of the so-called compensation behaviour and is a feature of the glass transition relaxation as studied by *t.s.d.c.*[2].

The structural relaxation or physical aging phenomena occurring in the glass transition region. has been investigated by studying the influence on the *t.s.d.c.* characteristic parameters of different annealing times, t_a, at several annealing temperatures, T_a, below the glass transition temperature.

It was observed that:

1- The intensity of the TC peaks decreases with increasing aging time;

The location of the TC peaks, T_m, slightly deviates to higher temperatures as the aging time increases;

The activation energy of the TC peaks decreases as the aging time increases.

These results suggest that, as the glass approaches the equilibrium state, *i.e.*, as the aging time increases, the power of the polarising electric field to activate molecular motions with high activation barriers decreases (the number of modes of motion that the field is allowed to activate decreases).

On the other hand, it was observed that the rate of the aging processes decreases as the aging temperatures decreases, suggesting that the search for deeper minima in the landscape of activation barriers becomes statistically more difficult as the temperature decreases.

We believe that the experimental results obtained in these aging studies clearly show that the so-called compensation behaviour is a mere consequence of metastability. Moreover, it is suggested that the difference T_c-T_g between the so-called compensation temperature and the glass transition temperature is a measure of how far the glass is from its equilibrium state.

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STATIC AND DYNAMIC DIELECTRIC PROPERTIES OF n-HEXYLOXY- AND n-OCTYLOXY- CYANOBIPHENYLS

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The studied compounds are the liquid crystals with the following sequence of the phases:

- crystal (58^0C) nematic (76^0C) isotropic - for n-hexyloxycyanobiphenyl (C_6H_{13}-O-Φ-Φ-C≡N, 6-OCB), and

- crystal (54.5^0C) smectic A (69.5^0C) nematic (79.5^0C) isotropic - for n-octyloxycyanobiphenyl (C_8H_{17}-O-Φ-Φ-C≡N, 8-OCB).

The importance of these compounds results from the fact, that in the mixtures of 8-OCB/6-OCB the stable reentrant nematic phase occurs [1-4].

The static permittivities ($e_{\equiv}$ end $e_{\wedge}$) were measured in the uniformly oriented liquid crystals by magnetic field (~0.8 T). The dynamic dielectric properties were measured for the orientation nşE, (i.e. for $e_{\equiv}$) in the frequency region: 100 kHz÷100 MHz.

The results are discussed in terms of

- **molecular structure**: a value of the angle between the long molecular axis and the dipole moment vector is determined on the basis of the static values of $e_{\equiv}$ and $e_{\wedge}$,
- **molecular aggregation**: the Kirkwood correlation factor value g<1 indicate the antiparallel pairing of dipoles,
- **molecular dynamics**: in the dielectric relaxation spectra the molecular rotations around the long and short axis can be distinguished.

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HEXASTAR-SHAPE CYCLOTRIPHOSPHAZENES AS KEY SUBSTANCES FOR DRUG DELIVERY SYSTEMS

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Polyorganophospazenes and their derivatives are known as termostable dielectrics, biocompable polyxners and Drug delivery Systems. Phosphazenes are suitable matrixes for modification of bioactive coropounds, their derivatives can posses own bioactivity for different fragments covalently bonded with main molecular skelettes [1]. On the other hand, high-ordered structures containing polyaminoacids and unique cyclic fragments (star-shaped polyrners with defmed tertiary structures) may produce new functional material using as selective membranes and biomedical compounds [2].

Early we have reported Synthesis and Study of various indolylalky-lamines bearing with tri- and tetracyclophosphazenes [3]. Hexa(kis)triptamine substituted cyclotriphosphazenes detect low toxity by tests in vivo (mouses, per os tabletts).

The preparation, properties and perspective application of new bioactive hexastar-shape cyclatriphosphazenes are considered.

Most promissory to study ionconductive, photoresponsible and luminescent properties of bioactive derivatives of cyclotriphosphazenes. We have obtained cyclotriphosphazenes covalently bonded with different triptamines and aziridine (mixed modifications). Ration of aziridine and triptamines (5-methoxy-, 5-nitro-, ?-methyl-) are concerned with solubility, bioactive level and toxic properties. DNMR method was applied to confirmation of star-structures of compounds. Stability of P-N bonds of heterocyclic derivatives cyclotriphosphazenes is studied by ionic blow (mass-spectroscopy method). Destruction of phosphazene cycle is shown, existing of fragments P-N from heterocyclic compounds, in particular, aziridine, is untypical for aminoorganocyclotriphosphazenes.

Immobilization of bioactive amines on cyclotriphosphazene to lead to new properties: anticancer activity, non-toxity, unstability of cyclophosphazene in physiological conditions (test in vivo, tablets are applicable). Hexasubstituted cyclotriphosphazenes are good objects for complexation with metals. Different possibilities for complexation with Pt(2+), Pt(4+), Co(2+) are discussed. Hexastarshape structures with central ring of phosphazene open new advantages for ionconductivity and transformation of metalloions.

Special interest is concerned with creation of new type polyaminoacid stars derivatives of cyclotriphosphazenes [4]. alpha-Helical conformation of polyaminoacid chains is necessary for delivery of specific substrates or enzymes to target. In this case influence of weak (physiological) electroconductivity (in solutions) on all System is discussed. Immobilization of functional Spiropyranes and dyes is possible on the end primary amino-groups of polyaminoacid fragments. Hexas tar-shape polyaminoacid derivatives of cyclotriphosphazene are key compounds for photosensitive or / and luminescent probes in biosystems as well.

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ELECTRICAL PROPERTIES OF DLC FILMS 1N THE METAL/DLC/SILICON HETEROSTRUCTURES

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During the last years the interest in diamond-like carbon (DLC) systems has been increasing due to their possible practical applications both in microelectronics and as chemically and thermally resistant coatings. The physical properties of DLC films strongly depend on their structure which results from the method of deposition and the conditions during deposition. In particular the electrical properties depend on the amount of sp2 (graphitic) and sp3 (diamond-like) chemical bonds and the relation between the two kind of bonding. The main aim of the investigations was to find the relation between the deposition parameters and the electric properties of MIS structures with diamond-like carbon as an insulator.

DLC films were deposited on n-type and p-type silicon wafers using radiofrequency plasma chemical vapour deposition (RF-PCVD) and pulsed cathode-arc discharge (PCAD). The measurements were carried out in the temperature range from 77 K up to 340 K in vacuum of the order of $5*10^{-5}$ Torr. The DC conduction was measured with Keithley 487 picoammeter working under Test Point software. The capacitance-frequency and capacitance-voltage measurements were carried out in the frequency range 10^{-2}Hz $\div 10^{5}$ Hz using Solartron 1260A Impedance Analyser with Chelsea Dielectric Interface. In order to confirm the diamond-like character of structures investigated the Raman spectra of some of the investigated samples were carried out.

The MIS diode forward to reverse rectification ratio is about two orders of magnitude. The dielectric measurements of the MIC capacitor show measurable dispersion in the frequency range used, probably due to the deep trapping levels.

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DIELECTROMETRY IN INVESTIGATION OF MOLECULAR LIQUIDS AND MIXTURES: STRUCTURE, SUPRAMOLECULAR ORDERING AND MACROSCOPIC MANIFESTATIONS.

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The results of recent developments on modeling of supramolecular ordering and dielectric properties of molecular liquids and mixtures have been reviewed. The main attention is paid to the approach based on a generalized quasichemical association model for a set of dielectric as well as thermodynamic and optical properties of liquids and mixtures, selforganized by specific bonding.

The hierarchy of theoretical models of nonideal mixtures of molecular aggregates is considered. The mixtures of molecular aggregates with differebt topology, polyvariant as regards structure and composition are discussed. The semimicroscopic theoretical approach for permittivity of mixrures, based on Frohlich results have been developed. The new interrelations between of permittivity and the thermodynamical and structural characteristics of supramolecular aggregation in mixtures were established.

Applications for analysing permittivity of series of molecular liquids and mixtures consisted by as alcohols, ketones, halogenalkanes, etc. have been presented The relationships derived allow quite detailed data to be obtained on the composition, structure and thermodynamics of aggregation, inaccessible by other methods particularly as regards long-range molecular correlations. The new data on the structure and thermodynamics of the aggregation in liquids and mixtures were obtained. Aggregation in molecular liquids and mixtures have been discussed in terms of the integral and differential parameters of aggregation. The long range molecular correlations, including ten or more molecules was established in liquids and mixtures in "usual" parameters of their state. The model of the aggregation describe and predict the permittivity in very wide intervals of the temperature ($\Delta T \cong 150$-200 K). The results have been applied also for calculations and analysis of thermodynamic functions of mixing, and coefficients of integral isotropic and anisotropic Rayleigh light scattering in mixtures. Macroscopic manifestations of supramolecular ordering in a set of the dielectric as well thermodynamic and optical physicochemical properties of molecular liquids and mixtures defined by different molecular parameters have been discussed.

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DIELECTRIC RELAXATION OF TRIOCTYLMETHYLAMMONIUM CHLORIDE

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The communication concerns the dynamic dielectric properties of trioctylmetylammonium chloride ('tricapryl-metylammonium chloride', Aliquat 336, TOMAC). This quaternary ammonium compound is a viscous liquid at ambient temperature and can be considered a kind of molten salt. As an amphiphile, it can act as cationic surfactant in solution. In the paper the results of the dielectric behaviour of pure TOMAC and in mixtures with the non polar solvents (n-heptane, iso-octane and 1,4-dioxane) are presented and the comparison to the results obtained previously for the electrolyte solutions [1,2] is made.

The dielectric loss of the liquid was measured in the frequency range between 100 kHz and 36 GHz at 20 °C (in case of pure TOMAC also at 50 °C). From 100 kHz to 10 MHz a HP E5050A dielectric probe (with HP 4285A LCR meter) was used which is advantageous in avoiding electrode polarisation effects. The loss spectrum of pure TOMAC at 20 ^{0}C is dominated by the conductivity contribution $\varepsilon''(\omega) \sim \omega^{-1}$, but in higher frequency region it exhibits a slop (in double log scale) of negative value <1, by this resembling the empirical Jonscher law [3]. To formally describe the results in the whole frequency range and to account for the reduced slope, an additional relaxational contribution of the Cole-Davidson type was introduced. However, careful examination showed that the fit can be much improved by introducing at lower frequencies a further spectral compound of the Debye type. Finally, the experimental data were analysed with conductivity term plus two relaxational terms.

$$\varepsilon''_{tot}(\omega) = \frac{\kappa_S}{\varepsilon_0\omega} + S_1 \frac{\tau_1\omega}{1+\tau_1^2\omega^2} + S_2\left(-I_m \frac{1}{(1+i\tau_2\omega)^\beta}\right)$$

where κ_S denotes the static (dc) conductivity, β is the Cole-Davidson parameter and S_i are the dielectric strengths.

The relaxation time of the lowest frequency term (τ_1) is found to be roughly related to the viscosity of the liquid in a manner similar to that observed as 'limiting' behaviour of many electrolyte (salt) solutions [4,5].

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SPACE CHARGE AND POLARIZATION DYNAMICS IN PVDF AND P(VDF-TFE)

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PVDF and P(VDF-TFE) are ferroelectric polymers with spatial distribution of polarization in thichness direction depended on the poling conditions. If either external charge is injected in the bulk during poling, or internal charge carriers are redistributed under action of the applied field, the uniformity of polarization will be distorted. Measurements of spatial distribution of space charge and polarization in ferroelectric polymers were usually performed on poled samples, reflecting the final state of the former and the latter. Here we present results on evolution or dynamics of polarization profiles obtained by 'in situ' measurements on 20 micrometer-thick extruded and uniaxially stretched PVDF and P(VDF-TFE) films poled at room temperature either in 'low' field of 60 MV/m, or in 'high' field of 180 MV/m. The coercive field was found to be around 50-80 MV/m. Profiles of polarization have been measured by the piezoelectrically induced pressure step (PPS) method about 100 times per second with resolution of 2 micrometer. In low fields, we observed growth of two symmetrical polarization peaks in PVDF indicating that redistribution of internal carriers predominated over an external injection, while only one peak near the positive electrode appeared in P(VDF-TFE) samples under the same conditions showing that the external injection of the negative carriers took place. When polarity of the poling field has been changed, polarization near the former positive electrode still remained in the same direction (has not been switched). Thus, the bimorph structure was formed. The equilibrium state after short-circuiting of the sample was reached in about 1 min, being in accord with the value of Maxwell's relaxation time. In the case of high poling fields, polarization was uniform during both the original poling and switching of the field polarity, except for narrow (2-3 micrometer) near-to-electrode layers where polarization abruptly dropped to zero. Attempts to improve uniformity of polarization in originally non-uniformly poled samples by applying the high field were not successful. The phenomenon was explained by effect of injected

and deeply trapped negative charge that prevented broadening of the polarized zone and switching the polarization. The experimental data were consistent with the model assuming interdependence of space charge and polarization, as stipulated by Poisson's equation. The space charge stabilizes the polarized state due to compensation of the depolarizing field, but, at the same time, it causes also non-uniformity of polarization. Our measurements and calculations proved that the trapped charge was localized macroscopically in transition zones separating polarized regions from non-polarized ones, thus compensating depolarizing field not only in individual crystallites, but in the whole polarized regions. Depending on poling conditions, the charge is trapped either near surfaces (high fields), or in the bulk (low fields). Except for the low poling field, the observed features were common both for PVDF and P(VDF-TFE).

FORMATION AND RELAXATION OF SPACE CHARGE IN CORONA POLED POLYSTYRENE

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Corona poling is a commonly used method for electrization of non-polar electrets, ferroelectric and non-linear optical polymers, but processes of formation and relaxation of space and surface charge deposited from corona are not fully understood. Since behavior of the space charge in polar materials is affected by polarization, we selected amorphous atactic nonpolar polystyrene (PS) for the present study. The 20 micrometer-thick samples were cast from solution and electroded from one side by vacuum evaporation of Al in a vacuum. The samples were poled in a corona triode at a constant current of 2 nA up to 2 kV at different constant temperatures T_p, while the kinetics of the surface potential was continuously recorded. Then the samples were subjected to the thermally stimulated depolarization (TSD) in one of three modes: with short circuited electrodes (SC), with the 3 mm-thick air gap (AIR), or with a PTFE 9 micrometer-thick spacer (SP). At 20-70°C, the potential kinetics curves were straight lines indicating that corona charge was accumulated on the surface of the dielectric. At T_p>80°C the curves became sub-linear due to injection of carriers. The best fitting was obtained with Rudenko-Arkhipov-Sessler's model assuming charge transport modulated by deep trapping. The product of carrier mobility and trapping time was found as 4.4×10^{-13} m^2 V^{-1} at 80°C. TSD-SC current in samples poled at 20-70°C did not show any peak, because surface charge was neutralized by short circuiting without producing an external current. The TSD-AIR current has shown a small negative peak at about 120°C and the TSD-SP current contained a very small positive peak followed by a large negative one. Positive peaks corresponded to the motion of charge towards the bare surface of the sample. At T_p> 80°C, the TSD-SC current shows a very sharp positive peak at 110°C, the TSD-AIR gives two negative peaks at 114 and 129°C, and TSD-SP current contains a broad positive peak at 117°C and a negative one at 132°C. The peak temperatures were higher than T_g=87°C proving that all were caused by charge

redistribution, and were not related to alpha relaxation. We solved numerically, at different initial and boundary conditions, the charge transport equations supplemented by Poisson and kinetic equations and assuming existence of the charge trapped partially at the surface and partially in the bulk and exponential dependence of apparent mobility on temperature. By fitting experimental curves to theoretical ones we obtained set of parameters for different conditions. As an example, in samples poled negatively at $80^{o}C$ we have found that space charge penetrated originally at about quarter of the sample thickness and then relaxed with activation temperature of 1.4×10^{4} K and pre-exponential factor 10^{42} m^{2} V s^{-1}. It has been found that the positive corona charge penetrates deeper in the bulk, than the negative one.

CORONA POLING OF A FERROELECTRIC POLYMER (PVDF)

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In ferroelectric polymers (FP), highly ordered and disordered phases coexist in one material. Corona poling is commonly used to obtain residual polarization, but processes of its formation and relaxation were not consistently studied so far. In this work we applied constant current corona poling to study potential buildup and polarization switching in PVDF and to find values of the residual polarization P_r and the coercive field E_c. Relaxation processes were studied by the thermally stimulated depolarization (TSD) current method. We studied biaxially and uniaxially stretched 10-30 micrometer-thick PVDF films poled in a specially designed corona triode. It has been found that the poling and switching processes consisted of three stages. The fast increase of the surface potential at the stage I indicated that the capacitive component prevailed in the poling current. At the stage II, there was a plateau at the voltage-time curve related, most probably, to switching of the ferroelectric component of polarization. The surface potential again increased sharply at the stage III when the switching was completed. Polarization was uniform in samples poled in dry air or at high field >100 MV/m. In humid air, saturation is observed due to a conductivity current. In fields of ~ 40 MV/m, polarization was distorted by injected charge. A new method was suggested to find the P(E) hysteresis curves and obtain static and dynamic dielectric constants, the coercive E_c and saturated E_s field. The method gives values of important parameters with all data obtained in one sequence of experiments and it can be used for any material with the hysteresis-like field dependence of polarization. For biaxially stretched PVDF we found $e_d = 7$, $e_f = 95$, E_c = 100 MV/m, E_s = 230 MV/m. We have found that the unstable part of the ferroelectric polarization is lost when poling is completed (4 mC/m^2). The residual and saturated polarization were correspondingly P_r = 64 mC/m^2 and P_s = 68 mC/m^2. For uniaxially stretched PVDF corona poled in normal humid conditions, we found the conductivity $g = 8\times10^{-14}$ Ohm^{-1}m^{-1}, $e_f = 40$, P_s = 42 mC/m^2 and E_c =48 MV/m. Obtained values are in agreement with the data reported in other studies. In order to distinguish between relaxation of the polarization and that of the space charge in

corona poled PVDF, we studied TSD currents 1 h and 14 month after poling. There were two TSD peaks after poling, but two additional peaks appeared on the samples stored for a long time. Our results indicate that probably four relaxation processes are involved, two associated with the dipole relaxation (in crystalline and amorphous phases) and other two related to the space charge. It follows from our results that very slow redistribution of charges and polarization takes place in ferroelectric polymers until the electret and ferroelectric components of polarization are finally separated, both accompanied by the trapped charges.

DIELECTRIC RELAXATION IN PVDF-$BaTiO_3$ POLYMER-CERAMIC STRUCTURES

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Polymer-ceramic structures have many common features with ferroelectric polymers. Both are two-phase materials composed of a highly disordered amorphous phase and a spontaneously polarized ferroelectric phase, however they differ in the scale of a structural non-uniformity. The structural similarity may also predetermine the commonness of dielectric relaxation processes. In this paper, relaxation processes in PVDF-$BaTiO_3$ composites were studied by several methods and results were compared with those known for neat PVDF. The 300 micrometer-thick samples were prepared by hot pressing of PVDF powder mixed with 10-micrometer ceramic particles with the content of $BaTiO_3$ from 40 to 70%. The thermally stimulated poling (TSP) was performed in the field of 4 MV/m. Thermally stimulated depolarization (TSD) currents were measured in the range from -160 °C to 0 °C on samples poled at room temperature and from -80 °C to +160 °C on samples poled at 150 °C. The fractional analysis of the relaxation seen at 20-150 °C was performed by the thermal windowing method with the window size of 5 °C. The AC dielectric spectra were measured at temperatures from -60 to +100 °C and frequencies from 100 Hz to 5 MHz. Four relaxation processes were identified, namely, the alpha relaxation in amorphous phase of PVDF, the beta relaxation in a glassy state of the polymer, the interfacial or space charge ? relaxation at 60-100 °C and the ferroelectric to paraelectric phase transition in $BaTiO_3$. The alpha relaxation was seen as a broad non-Debye peak at -45 °C at the TSD curves having characteristic activation energy of 0.54 eV, and as a peak at -20 °C and 50 kHz at the frequency dependence of the imaginary part of the dielectric constant. Havriliak-Negami's model was fitted to the experimental data, indicating asymmetry of the peak caused by a difference between interclaster and intraclaster interactions of dipoles. The beta peak appeared at -135 °C at TSD current curve. Thermal windowing of the high temperature TSD peak revealed that the activation energy of individual processes decreased in the range of 20-80 °C from 1.17 to 1.09 eV, but then it increased sharply reaching a maximum at 105-110 °C, from 1.23 to 1.55 eV depending on composition. The TSP experiments indicated that the apparent conductivity abruptly decreased at 70-80 °C, probably because of the deep trapping of charge carriers at interfacial boundaries. The phase transition in the filler was seen as an elbow at 120 °C at the TSP curve and as a splash of current during both heating and cooling in TSD experiments. Thus, it has been shown that relaxation processes in the PVDF-$BaTiO_3$ polymer-ceramic structure are similar to those in a ferroelectric polymer (PVDF). One can considered this as a pre-condition for development of the generalized physical model applicable to both classes of materials.

LOW-FREQUENCY DIELECTRIC PROPERTIES OF HIGH-RESISTIVITY GaSe LAYERED CRYSTALS

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Gallium selenide belongs to materials which crystallize with layered structure. Withing a layer the binding between atoms is covalent; between layers it is of the van der Waals type. The peculiarities of crystal structure cause interesting optical and electrical properties of this material.

One of them is a high density of localized states in the energy gap close to Fermi level, which are caused by presense of the defects of crystal structure such as vacancies, interstitial impurities and layers' stack faults. Consequently, the band structure of layered crystals is like as amourphous ones, that allows to investigate them by dielectric spectroscopy method with the purpose to study the dynamics of charge carriers localized on the deep levels. Till now few papers are devoted to studies of low-frequency dielectric response in gallium selenide, especially in wide frequency range. That is why in this work the dielectric response of high-resistivity GaSe-layered crystals (~107 cm at room temperature) along c-axis have been studied in the 20 Hz - 100 kHz frequency range at 240-293 K temperatures. Crystals for studies grown by Bridgman-Stockbarger method were cloven along layers with thickness less than 1 mm. Indium contacts soldered on both fresh cloven surfaces were used as capacitor plates. The measurements were carried out by transducing of capacity into voltage; applied to samples ac RMS voltage was not exceeding 100 mV.

The slight dispersion of C' capasity is observed over almost all frequencyrange; dc-loss with -1 slope prevails on frequency dependence of imaginary part of capasity - C". Non-linear distorsion of sine current has not been observed either at 100 mV or 1V RMS even on lower frequencies that confirms the volume character of dielectric response.

Reduced data at 293 K after substraction of relevant magnitude of dc-loss show fairy good agreement to K-K compatibility obeying to "universal" power law of spectra with 1-n = 0.20 slope. Such behavior of response is typical to Austin-Mott model for ac hopping conductivity on localized levels close to Fermi level .

The dielectric response of samples with different thickness (0.8, 0.4 and 0.2 mm) cloven in proximity one to another have been compared with the aim to identify volume or barrier character of polarization. The capacity increases reciprocal to samples' thickness at the highest frequencies of the measured range. But at lower frequencies on thin samples (0.4, 0.2 mm) some anomalous changes of spectra take place.

DIFFERENT MOLECULAR MECHANISMS FOR THE DIELECTRIC HYSTERESIS AND THE PYROELECTRICITY IN A POLY(VINYL ALCOHOL) WITH AZOBENZENE-ALKOXY SIDE CHAINS

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After thermal poling, pyroelectricity and a pronounced dielectric hysteresis have been observed on films of a poly(vinyl alcohol) with azobenzene-alkoxy side chains. Together with donor and acceptor groups that are linked by its delocalised π-electron system, the azobenzene group forms a strong A-π-D dipole. Pyroelectrical measurements, dielectric spectroscopy and differential scanning calorimetry have been used in order to determine the contributions of the A-π-D dipoles to the pyroelectricity and to the polarisation charge.

The pyroelectric activity can be explained with reversible dipole-density changes upon thermal expansion. Assuming a perfect orientation of the side-chain dipoles, the maximum possible pyroelectric coefficient is calculated from the temperature dependence of the susceptance at temperatures where all the dipoles are immobile. Using the experimentally determined pyroelectric coefficients, this allows for a calculation of the avarage tilt of the side chain dipoles. Because of sterical hindrance the thermal poling is not very efficient.

The dielectric hysteresis is proposed to result from the polarisation caused by charge carriers. This is deduced from a comparison of the maximum theoretically possible dipolar polarisation and the experimentally determined value, assuming that the sample consists of just one macro-domain. Furthermore, the observed low frequency relaxations with huge dielectric losses can only be explained with a charge-carrier polarisation; the strong low-frequency dispersion points toward an ionic conductivity. These findings are also significant for the interpretation of dielectric-hysteresis measurements on other polymer-electret materials.

ELECTRICAL PROPERTIES OF POLYIMIDE

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In this work, electrical conduction characteristics of polyimide film with aromatic ring after electron beam irradiation were studied. It was irradiated in air at room temperature at JAERI with four kinds of doses: 5, 50, 75 MGy and 100 MGy. Electrical strength of 0.2 MV/cm was applied to unirradiated and irradiated polyimide and conduction current was measured from room temperature to 250°C. ESR spectrum of unirradiated and irradiated specimens was measured.

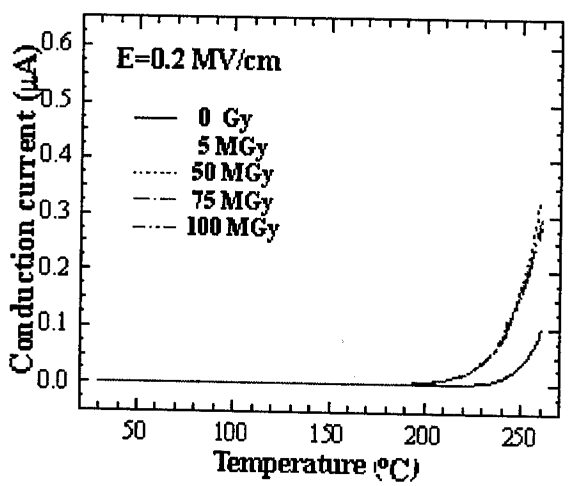

Fig. 1 Temperature dependence of conduction current.

Fig. 1 shows the temperature dependence of conduction current at different dose. Conduction current of 50, 75 MGy and 100 MGy irradiated specimen increased slowly with increasing the temperature and it increased above about 210°C rapidly. Conduction current of unirradiated specimen increased above about 240°C rapidly. The temperature at which this current increases rapidly shifted to a lower one with increasing the dose. On the other hands, conduction current of irradiated specimens became larger than that of unirradiated ones above about 200°C. From results of ESR spectrum, it was found that free radicals increased with increasing the dose.

However, there was no difference between irradiated specimens expect for 5 MGy irradiated ones. Therefore, it is considered that since the molecular bonds in the amorphous region are cut out owing to electron irradiation, ions increase with increasing the dose.

These results are different from those of polyetheretherketone[1] that belongs to aromatic polymer.

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CORRELATION BETWEEN CONDUCTIVITY AND DIELECTRIC SPECTRA IN HYDROGEN BOUND FERROELECTRICS.

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The existance of two fundamentally different types of dielectric behavior, associated with 1) dipolar material and 2) slowly mobile ionic or electronic charges, as the basic idea of the universal dielectric dispersion law was ellustrated by dielectric spectra of hydrogen bound ferroelectrics. Two most typical ferroelectrics, triglycine sulphate and Rochelle Salt, were choosen for investigations.The dielectric spectra of both crystals were measured together with their conductivity in a wide temperature and frequency range. The correlation was revealed in the temperature behavior of both dc and ac conductivities and dielectric spectra. In the vicinity of phase transition temperature the sharp raise in conductivity was followed by the appearance of an additional mechanism of dielectric dispersion.

ELECTRICAL AND MECHANICAL PROPERTIES OF STYRENE-BUTADIENE RUBBER REINFORCED WITH SYNTHETIC FIBER

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A systematic electrical and physico-mechanical properties of styrene butadiene rubber (SBR)/Polyester short fiber (PE) loaded with fast extrusion furnace carbon black (FEF) in increasing quantities are reported.

The dielectric measurements were carried out at a frequency range from 100Hz to 10 MHz at temperatures between 30 and 60°C. Also the resistivity at the different temperatures for the investigated samples was studied. The effect of natural and thermal ageing of the same samples on the electrical and mechanical properties have been investigated. The results are discussed and interpreted.

DIELECTRIC AND PHYSICO-MECHANICAL PROPERTIES OF EPDM/NR BLEND LOADED WITH DIFFERENT CARBON BLACKS

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Ethylene-Propylene Diene terpolymer Rubber/Natural Rubber blends (EPDM/NR) in different proportions (100:0, 75:25, 50:50, 25:75 & 0:100) reinforced with 20 phr Semi-Reinforcing Furnace carbon black (SRF) have been studied. The permittivity ε' and dielectric loss ε" for these samples were determined in the frequency range 10^2-10^7 Hz. Also, their physico-mechanical properties were investigated.

The blend EPDM/NR (75:25) possessed the best mechanical properties and stability against aging. So, it was chosen to explore the effect of adding carbon black in different quantities up to 50 phr on its electrical and mechanical properties. Three different types of carbon black, namely, HAF, FEF and MT were used. At certain concentration of carbon black, referred to as the threshold percolation concentration, an abrupt increase in ε' and ε" depend upon its type was detected. This could be attributed to some sort of interaction between the blend and the carbon black at higher concentrations.

DIELECTRIC PROPERTIES OF ANTIFERROELECTRIC LIQUID-CRYSTALLINE MIXTURES

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Dielectric spectroscopy is an efficient tool for investigations of the long-range dipole order in liquid crystals. It delivers also information on the dynamics of collective and non-collective molecular processes in chiral smectics. We used this method for the characterisation of new mixtures, possessing antiferroelectric C_A^*-phase in a broad temperature range. The antiferroelectric phase in these mixtures is extended down to below the room temperature. The investigated mixtures possessed also ferroelectric smectic C* and paraelectric smectic A phases. In all investigated materials we observed two absorption peaks in the existence range of the antiferroelectric C_A^*-phase, lying in the kHz-MHz range of frequency. Both peaks are quite week and of Debye type. Their characteristic relaxation times are almost temperature independent. The small intensities of the observed absorption peaks prove that they are not attributed to any of collective relaxation processes. We suppose, the peaks are related to the motions of molecules on a cone, defined by tilt angle of molecules in smectic layers. The slower process is probably related to the motions of molecules, tilted in opposite directions in subsequent layers, and moving in the same direction. The process with shorter relaxation time is attributed to the movement of molecules in opposite (anti-phase) directions. Both modes are active in dielectric measurements due to small residual polarisation being a consequence of the helical superstructure.

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SWITCHING BEHAVIOUR OF ANTIFERROELECTRIC LIQUID-CRYSTALLINE MIXTURES

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Antiferroelectric liquid crystals seem to be very promising materials for liquid-crystal displays. Without electric field, the molecules in subsequent smectic layers are tilted in opposite directions. In the presence of strong electric field, the molecules in all smectic layers are tilted in the one direction, which can be switched by 180° by changing the field direction. Hence, antiferroelectric liquid crystals exhibit tristable switching with distinct thresholds. On the other hand, they offer the possibility of obtaining the grey scale in a simple way.

We studied the switching behaviour of some mixtures, possessing the antiferroelectric C_A^*-phase in very broad temperature range, including the room temperature. We detected the switching phenomenon using two independent methods. In the electrooptic method, the intensity of light passing the sample placed between crossed polarizers was registered as a function of the applied electric field strength. In the second method, we registered the polarisation current flowing across the cell during the change of polarisation direction. Both methods have given consistent results. The critical electric field strength needed for changing the polarisation direction by 180° has been determined as function of temperature, pulse shape and frequency. The tilt angle of molecular long axes with respect to the smectic layers normal was measured using an electrooptic method. The tilt angle and the switching time were determined as functions of temperature.

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IN-SITU ELECTRICAL ANALYSIS IN VIEW OF MONITORING THE PROCESSING OF THERMOPLASTICS

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In the last recent years, electrical techniques like microdielectrometry have presented an attracting and increasing interest for continuous monitoring, in a nondestructive way, of the advancement of the reaction of thermoset resins under cure. We think that the use of electrical analysis for in situ monitoring of chemical reactions can be extended to get information on thermoplastics and the physical phenomena such as crystallization (1) or study of residence time in processing machines such as extruders.

Recently some studies were conducted for this purpose and concerned the changes in the long range motions occuring above the glass transition temperature due to the growing of the crystals during isothermal crystallization (2-4). On the other hand, as far as the electrical properties are concerned, the effect of the crystallinity is to lower the ionic conductivity. This conduction was frequently invoked to account for the low but finite conductivity of many of the more insulating polymers especially in the melt state (5,6). We discuss in this paper how we can follow by in situ electrical analysis the influence of the crystallization on the dipole dynamics and the charge migration. This last phenomena can be also used to control the mixing and to evaluate the residence time of a polymer in an extruder.

Concerning the monitoring of crystallization, the analysis were carried out on a polyamide and a polyvinylidene fluoride directly in the cell of a dieletric spectrometer or in a modified rheometer where the plates were connected with an impedance analyzer.

The study of the residence time was conducted on a polyethylene. In a first time the conductivity of this polymer in the melting state was analyzed in function of the amount of ionic salts incorporated at low contents. On this basic study, we have defined a critical amount of ionic salts which can be used to prepare a master blend. The die of an extruder was equipped with an electrical sensor linked to an electrometer. Different types of feeding of the extruder with the probe were tested (Dirac or step) for two designs of the screw.

The results of the behavior of the conductivity during crystallization are in accordance with the thermal analysis and with the evolution of the complex mechanical shear modulus. A comparison of the transformation ratio obtained by the different experimental methods is reported.

In the extruder, we show clearly that the residence time is proportional to the flow rate and that the increase of this flow rate modifies the capacity of mixing of the screw. The introduction of different mixing elements (Maddock, pineapple) is marked by a binodal distribution of the residence time.

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THERMALLY STIMULATED DEPOLARIZATION CURRENTS IN LOW DENSITY POLYETHILENE FILMS

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Thermally stimulated depolarization (TSD) currents (Fig.1) and fractional thermalle stimulated depolarization (FTSD) currents (Fig.2) in low density polyethilene films with thickness 12-50 μ in temperature interval 20-110^{0}C were investigated.

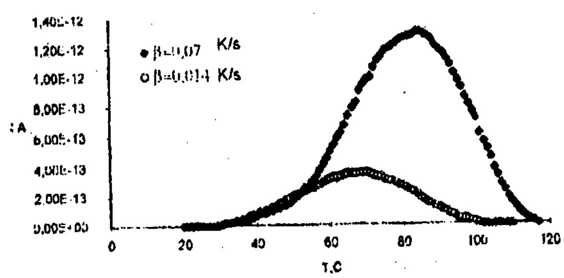

Fig 1.

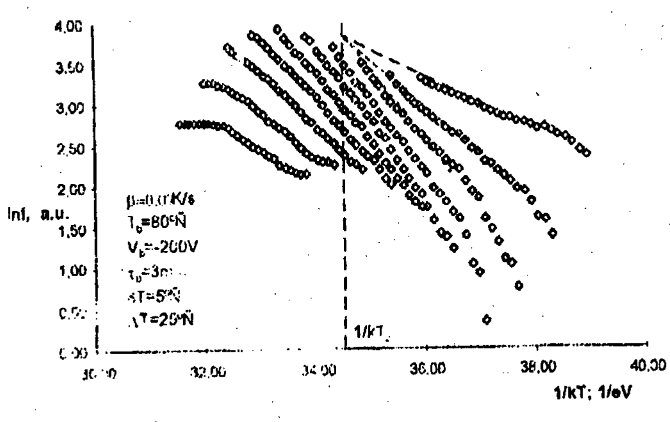

Fig 2

FTSD data development proves the xeistence of a broad energy spectrum of electrically active defects (EAD) in the 0,3-0,95 eV range.

Low temperature FTSD fraction in coordinates Ln I from 1/kT look like straight lines crossed in one point. This is the evidence of the compensational law fulfillment which allowas to define the compensation temperature T_c=336,3 K (Fig.2).

TSD data development measured at two constant heating rates β *(Fig.1)* by Tikhonov regularization method with the use of integral equation on the type:

$$J(T) = w_0 \int_0^{K_m} G(E) \exp\left[\frac{E}{k}\left(\frac{1}{T_c} - \frac{1}{T} \right) - \frac{w_0}{\beta} \int_{T_0}^{T} \exp\left(\frac{E}{kT_c} - \frac{E}{kT'} \right) dT' \right] dE$$

where G(E) - EAD distribution function along the activation energy, w_0 formal parameter, allowed to restore the function of EAD energy distribution G(E), the wide maximum of which in the interval 0,3 to 1,2 eV possesses the most probable energy of 0,73 eV in the material under investigation (Fig.3).

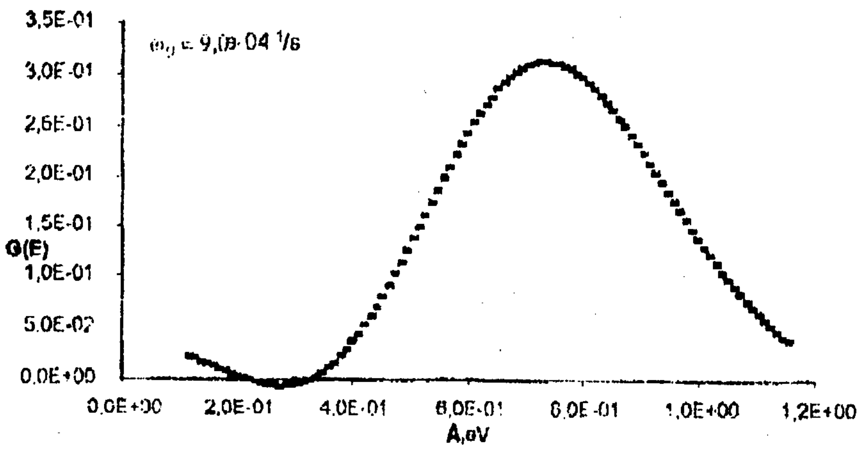

Fig 3

Eu AND Tm DOPED LITHIUM TETRABORATE (LTB) CRYSTALS AS MATERIAL FOR THERMOLUMINESCENCE DOSIMETERS.

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In last time research has been concentrated on borate system. Lithium tetraborate is a perspective material for thermoluminescence dosimeters.

Thermostimulated luminescence (TSL) of pure and Eu and Tm doped $Li_2B_4O_7$ single crystals in temperature interval 290-600 K has been investigated. Curves TSL at different doses of X-ray and γ-irradiation were obtained and the depth of capture levels of current carriers has been calculated for following maxima: 420, 473 and 548 K (0.84 eV, 0.95 eV and 1.1 eV respectively) It was established that doping by Eu favoures an increase of traps number with E=0.95 eV and E=1.1 eV and hiders the trap formation with E=0.84 eV. Tm-doped crystals exhibit an opposite case. The possible centers of luminescence are discussed. The double activation in LTB: Eu, Gd has been investigated too. It was ascertained that the probability of concentrative extingnishing of radiative recombination is increased in parallel with the irradiation dose. Basing on analysis of TSL curves, intrinsic defects (vacancies, autolocalizational exitons and other) and dopant ions have been supposed to render a strong mutual influence in $Li_2B_4O_7$ crystals.

INFLUENCE OF SPACE CHARGE ON LIQUID CRYSTAL DIRECTOR DYNAMIC

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The electrooptic effects in the vicinity of the pores of a dielectric film of silicon-dielectric film -nematic(5CB, $\Delta\varepsilon$>O)-ITO structure under the action of the AC voltage have been investigated. The cell thickness was 20 μm. The average size of the pores of dielectric film is about 10 μm. An initial orientation of director was homeotrop. A reorientation of liquid crystal director takes place if the cell was earlier under the action of DC voltage with "-"U polarity on silicon only. The deformed region of liquid crystal layer has the following properties: a) axial symmetric view(0°-360°) with its center at the pore of dielectric film, b) the size(diameter) of this region is about 150-200 μm, c) optical trace disappeare during several minutes, d) the frequency region of the electrooptic efiect existence is extended from several Hz to 2,5 kHz, e) switching between any two different frequencies causes the change of the optical trace with responce time about 10 ms.

It is shown that experimental data cannot be explained by dielectric, flexoelectric or surface polarization electrooptic effects.

It is supposed that in the visinity of the pores of dielectric film a positive space charge which accumulated earlier induces the dimers of liquid crystal molecules. In this case coupling between AC electric field and quadrupole of dimers is responsible for a discussed electrooptic effect.

TEMPERATURE AND PRESSURE STUDIES OF DIELECTRIC PERMITTIVITY IN THE NITROBENZENE - n-ALKANES BINARY MIXTURES

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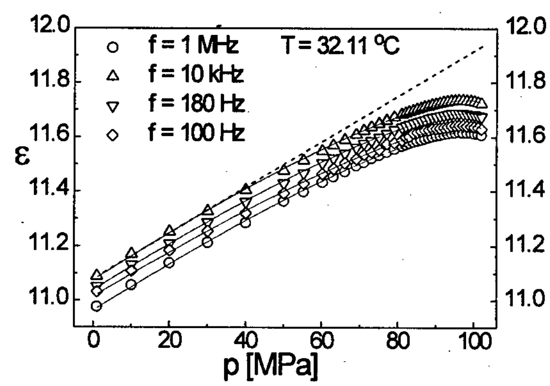
We present results of pressure studies of dielectric permittivity ε on approaching the critical consolute point (CCP) in a nitrobenzene - n-alkanes binary mixtures for frequencies varying from 1 MHz to 100 Hz. It has been found that the critical behaviour of ε is well portrayed by the relation:

$$\varepsilon = \varepsilon_c + C^p \widetilde{P} + C_1^p \widetilde{P}^{1-\alpha} + \dots$$

where $\widetilde{P} = P_c - P$ is the pressure distance from the CCP, $\alpha \approx 0.12$ is the critical exponent which describes the singularity of the specific heat.



Pressure dependence of dielectric permittivity in a near-critical nitrobenzene-dodecane solution for the isotherm remote from the critical temperature under atmospheric pressure by $\Delta T = 5\ K$.

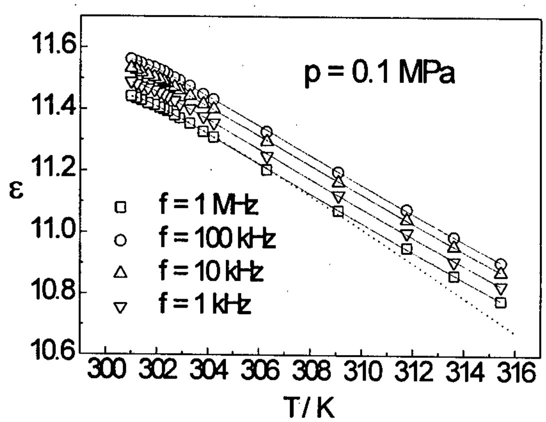
This relation, proposed by Sengers *et al.* [Physica **104A** 1980], is isomorphic to that applied in studies under atmospheric pressure:

$$\varepsilon = \varepsilon_c\left(1 + Ct + C_2 t^{1-\alpha} + C_3 t^{1-\alpha+\Delta_1} + \dots\right) \qquad T>T_C$$

where: $t = |(T- T_C)/T_C|$, T_C is the critical consolute temperature, ε_C is the value of dielectric permittivity at the critical point, C_1, C_2, C_3 are amplitudes, Δ_1 is the first correction-to-scaling exponent. This model also gave the form of the critical amplitude:

$$C_1 = -s_C s_C^{+} \rho_C \left(\frac{2}{\varepsilon_0} \frac{dT_C}{dE^2} + \varepsilon_C \frac{dT_C}{dp} \right)$$

where: $s_c\, s_0^{+}$ is the critical amplitude in the expansion of the molar entropy s.
The presented in this report results were conducted both in solutions with positive (nitrobenzene-dodecane) and negative (nitrobenzene-hexane) values of dT_C/dp. Additionally, in these solutions values of dT_C/dE^2 have been determined, using the method based on the nonlinear dielectric effect technique.



Temperature dependence of dielectric permittivity in a near-critical nitrobenzene-dodecane solution. For the frequency of 1 MHz a fit without a correction to scaling was shown (dashed line).

The weakness of the pretransitional anomaly of ε in the isobaric, temperature studies is clearly visible. New features of the critical effect for the isothermal, pressure path in comparison to the temperature studies under atmospheric pressure have been found:

- no correction to scaling terms were applied,
- Maxwell - Wagner effect wasn't noticed even for a frequency as low as 100 Hz,
- the isothermal, pressure anomaly of ε is much stronger than the isobaric, temperature anomaly of ε.

Studies were supported by the Committee for Scientific Research (KBN, Poland), project Nr 2 PO3B 101 13.

INFRARED AND RAMAN SPECTROSCOPY OF SINGLE CRYSTAL AND TEXTURED GLASS CERAMICS OF $LaBGeO_5$

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$LaBGeO_5$ is a new ferroelectrics which exhibits order-disorder ferroelectric phase transition at T_c = 793 K. Dynamics of the phase transition in crystalline $LaBGeO_5$ was studied using submilimetre and infrared reflectance spectroscopy in the frequency range 4-2000 cm^{-1} (at temperatures 300-873 K) . Most of the phonons exhibit classical temperature behaviour – their frequencies slightly decrease on heating. However, the phonon at 87 cm^{-1} (300 K) in E||c spectrum (A-symmetry) shows pronounced anomalous softening down to 59 cm^{-1} at Tc. Another phonon of the same A-symmetry exhibits softening from 143 to 115 cm^{-1} in already published Raman spectra (R.V. Pisarev and M. Serhane, Solid State Physics 37 (1995) 3669). It seems that the phase transition is driven by the phonon softening and the phase transition is of mixed order-disorder and displacive type. We have performed also Raman scattering experiment on textured glass ceramics and a strong boson peak was observed near 70 cm^{-1} at room temperature.

THE EFFECT OF THE ADHESION SYSTEM (HRH) ON THE PHYSICO-MECHANICAL AND ELECTRICAL PROPERTIES OF SBR/POLYESTER SHORT FIBER COMPOSITES

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Short fiber attracted the attention of several researchers due to their good dispersion as well as their advantages on the physico-mechanical and dielectric properties. This work represents a systematic study on the electrical and physico-mechanical properties of styrene-butadiene rubber reinforced with polyester short fiber. Next, to point out the influence of adhesion system: HRH (hydrated silica, resorcinol and hexamethylene-tetramine), the fiber concentration and ageing on these properties of the investigated samples. The obtained data are discussed and interpreted.

APPARATUS FOR DIELECTRIC RELAXATIONS MEASUREMENTS IN LOW FREQUENCY RANGE

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The concept of the new method of apparatus with the use of active inductor is presented.

A dielectric sample is connected parallel to terminal of inductor, which inductance is very big. The sample is charged by dc voltage battery and next it discharges by input terminals of inductor which is represented by inductance and parallel resistance.

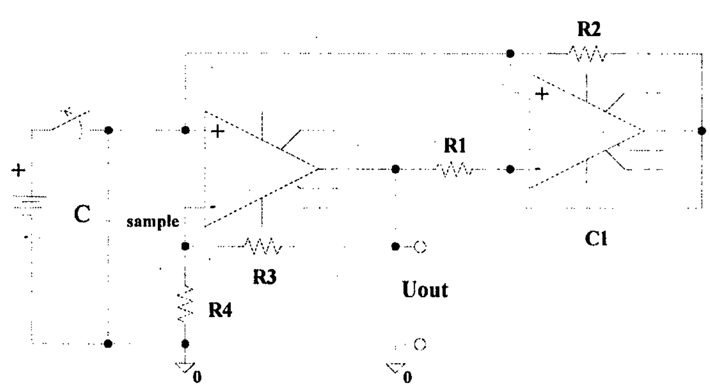

Fig1.) Schematic diagram of the apparatus.

AC voltage which represents founded solution is observed on oscilloscope and registered by digital multimeter KEITHLEY DMM 2000.When the solution is periodic, from the value of frequency the sample capacitance is calculated and from logarithmic decrement the parallel resistance of the sample is achieved.

The inductor is realized according of Riordan concept. Two special operational amplifiers and some RC elements make it possible to set the inductance value about 10^{12} [H].

Properties of this inductor vs. frequency was design by computer simulation in SPICE program. This apparatus was used for dielectric relaxation measurements in resin (epidian) and glasses.

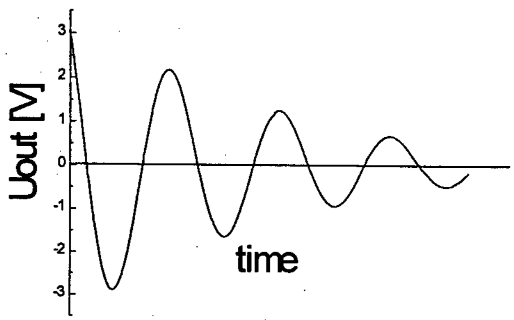

Fig2.) Block diagram of the apparatus.

PHOTOCONDUCTIVITY OF PERYLENE LAYERS

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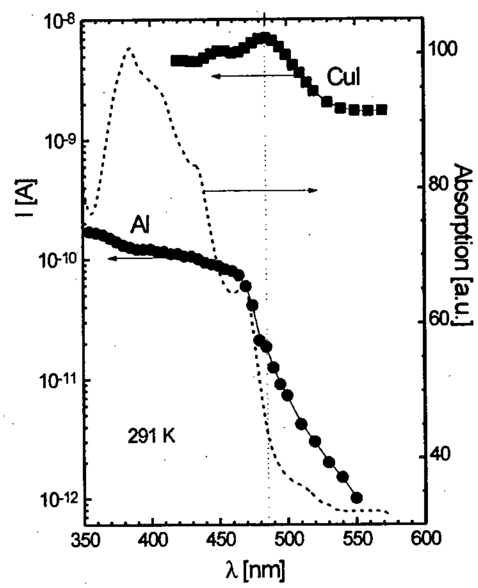
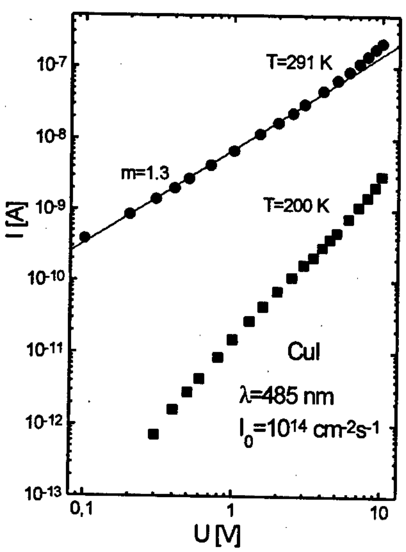
In spite of anthracene, tetracene and pentacene the photoconductivity as well as the process of photogeneration of charge carriers in perylene are not well known [1, 2, 3, 4].

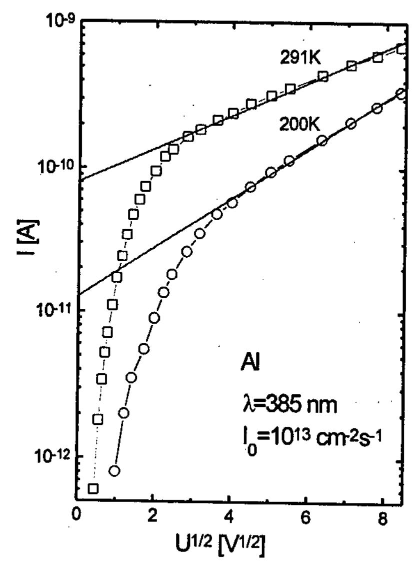
Our experimental investigations were carried out on vacuum-evaporated polycrystalline perylene layers about 1-6 μm thick provided with electrodes effectively (CuI) or poorly (Al) injecting holes. We measured the dependences of current on electric field and temperature both without illumination and in the presence of illumination by light from the singlet-absorption range of perylene. Moreover, by way of experiments we obtained the photocurrent as a function of wavelength and light intensity. The examples of spectral and voltage characteristics of photocurrent obtained on the layers of 5.2 μm are presented in Figs. 1, 2 and 3. In the case of the sample provided with CuI electrodes there is a peak of photocurrent at λ=485nm, which is reflected neither in the absorption spectrum of perylene nor in photocurrent spectrum obtained for the samples provided with Al electrodes.



Spectral characteristics of photocurrent for the sample provided with Al electrodes or with CuI electrodes and absorption spectrum of perylene layers.

Such a behaviour of current confirms the occurrence of a photoenhanced current flowing in the presence of CuI electrodes [3, 4]. However, in this case the photocurrent-voltage relation can be written as $j \sim U^m$ with $m=1.3<2$ (Fig.2), which is not in agreement with Helfrich model. The value of m ($m<2$) can result either from generation of charge carriers via impurity centers [4] or from charge carriers diffusion, which was neglected in Helfrich theory for thick crystals but eventually important in the case of thin layers.





Photocurrent-voltage characteristic for two values of temperature for the sample provided with CuI electrodes

Photocurrent-voltage characteristic for two values of temperature for the sample provided with Al electrodes

For the layers with Al electrodes the photocurrent was proportional to light intensity of λ=385nm. For respectively high voltage the photocurrent-voltage relation can be written as log $j \sim U^{1/2}$ (Fig.3). The apparent activation energy of this photocurrent yields 0.13eV. Assuming Schottky emission model we can calculate the dielectric constant, ε=6.1±0.5, from linear parts of both characteristics in Fig.3 [5]. Such a value of dielectric constant seems to be to high. Therefor , other mechanisms of charge carrier generation should be considered.

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Acknowledgment

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A FRACTAL INTERPRETATION OF THE DIELECTRIC RESPONSE OF DOPA-MELANIN BIOPOLYMER .

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Melanins are known as organic amorphous semiconducting biopolymers with important physico-chemical properfaes including easy formation of charge transfer complexes, strong cation binding, stable radical properties, phonon-photon coupling and wide spectral absorption [1]. The presence of natural melanins in both illuminated (skin, hair, eye) and non-illuminated (substantia nigra of the brain, stria vascularis of the cochlea) areas indicates that their biological function is not restricted to the photoprotective action only.

Dielectric measurements have been performed on synthetic dopa-melanin obtained by oxidation of L-3,4-dihydroxyphenylalanine (dopa) using two impedance analyzers: a HP 4192A Impedance Analyzer in the frequency range 100Hz-I0MHz and HP 4191RF Impedance Analyzer in the range 1-1000MHz.

Real and imaginary components of the dielectric permittivity show an anomalous low-frequency dispersion [2,3]. According to the cluster model of the dielectric response [4] at frequencies $\omega > \omega_c$ (ω_c crossover frequency) potentially mobile charges correlate their individual displacements to generate a coherent charge displacement identified as a polarized cluster. Two values of the index n for melanin: 0.3 and 0.8 can be attributed to the formation of two different clusters as the frequency is changed. The value near unity for p (p=0.93) in the frequency region $\omega < \omega_c$ indicates a quasi-d.c. process, in which charge movement between clusters takes place relatively freely with a large path length between jumps.

Melanin granules are porous aggregates formed in the colloidal melanin suspension upon reducing pH. Huang et al. [5] used light scattering techniques to study the dynamics of the aggregation. They found fractal structure of aggregates and two regimes of aggregation, one corresponding to the diffusion limited aggregation with fractal dimension of d_s=1.8 and the other one corresponding to the reaction limited aggregation with fractal dimension D_p 2.2. Analytically solvable fractal circuit models, e.g. the self similar branched porous electrode system, are found to be equivalent to the cluster model [6]. According to this model, the clusters are to be taken as the internally self similar pores and the cluster distribution referes to the fractal arrangement of the pore cross-section.

Assuming that d_s is related to the surface dimensionality of the pore system in melanin and according to the porous electrode model, we can express the index p as follows: $p=/1-d_s/$. For melanin p and d_s are equal to 0.93 and 1.8, respectively, so that the relation is fulixlled quite well. In the frequency range $\omega>\omega_c$ the index n can be expressed by the relation: $n=3-D_p$, where D_p is the fractal dimensionality of the internal pore surface. Taking D_p as equal to 2.2 we found that n=0.8, which is in very good agreement with one of the indexes n obtained from the dielectric response. On the basis of the recent data concerning the fractal nature of melanin it is difficult to interpret the second value of the index n equal to 0.3. However, more than a single value of n is allowed in the fractal model of the low frequency dielectric response [6].

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RELAXATION PHENOMENON AS A COMPOUND BERNOULLI SCHEME.

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In the traditional attempt to relaxation phenomena it is claimed that the relaxation process at each instant of time t follows the Bernoulli scheme in which the success occurs when the particle has relaxed before the time t what happens with probability $p(t)$. It is considered also that the relaxation function $\phi(t)$ given by experiments is simply equal to the fraction of number $N(t)$ of species not relaxed at time t from $N(0)$ species being at the initial time in the state imposed by external constraints. In this paper we ask the following question: does this model of relaxation phenomenon reflect fully the complexity of relaxing systems?

In the special case when the number $N(0)$ is determined and large, it follows from the strong law of large numbers that the fraction of unrelaxed species at time instant t is asymptotically equal to the probability that one single particle has not relaxed yet at time t, i.e. to the probability $1 - p(t)$ that the success does not occur. Hence, the definition of the relaxation function by means of this fraction does not take into account the properties of relaxing system in full extent and cannot explain the universality observed in the relaxation processes on the macroscopic level of the system. Moreover, although the relaxation function given by experiments is deterministic, both numbers $N(0)$ and $N(t)$ at each instant of time - and hence the fraction of unrelaxed species - are, in general case, not determined and seem to be random variables with the probability distributions depending on the number of all species in the system. Consequently, the traditional attempt to relaxation seems not to include whole the complexity of the relaxing systems.

We propose, therefore, a generalization of traditional model more adequately describing the complex systems. Namely, at each instant of time t we consider the relaxation phenomenon of a complex system as a compound Bernoulli scheme with the unknown, random number $N(0)$ of trials and the probability of success $p(t)$, both depending on the number of all species in the system. Then, we define the relaxation function $\phi(t)$ as a probability that the system (not only one single particle) has not relaxed yet at time t, that is achieved when the number of successes in the sample equals 0. Thus, $\phi(t) = Pr(N(0) - N(t) = 0)$ what equals $(1 - p(t))^{N'}$ given $N(0) = N$. Finally, we show that this definition coincides with so-called first passage of the system proposed and discussed earlier.

THERMOLUMINESCENCE STUDY OF POLY(METHYL-PHENYLSILYLENE)

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Disordered polymeric photoconductors are of both technological and fundamental interest due to their application in electrophotographic, electroluminescent and photovoltaic devices. It is commonly accepted that charge carrier transport properties in these materials can be described in the framework of the Gaussian Disorder Model. The present report is devoted to our recent thermoluminescence (TL) study of poly(methyl-phenylsilylene) (PMPSi) as well as some other polysilylenes over the wide temperature range from 4.2 to 350 K, and to further development of recently proposed approach [1] using the fractional TL-technique for probing the energetic disorder of localised states. Interpretation of low-temperature TSL of PMPSi as associated with charge carrier thermal release from intrinsic tail states of the DOS distribution is suggested [2]. Such approach based on the Gaussian disorder model provides reasonable understanding of all observed trends in the TSL. According to this, the shape of the high-temperature wing of the TSL peak and the energetic position of its maximum could be explained consistently incorporating the concept of the transport energy. The above characteristics of the TSL peak are determined by the energetic disorder parameter of the system. It was shown that the position of TSL peak maximum is in accord with predictions of the theory for non-activated energetic relaxation of photogenerated carriers within a Gaussian shaped manifold of localized states, and, therefore, no features of the DOS in the gap are necessary for existence of the low-temperature TSL peak. Whereas the appearing of deep extrinsic traps of photodestructive origin is responsible for a new high-temperature TSL peak. in PMPSi. The problem of photodestruction of PMPSi is also discussed.

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NONLINEAR DIELECTRIC RELAXATION IN DIPOLAR SYSTEMS

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Electric field of high intensity ($\geq 10^6$ V/m) applied to polar liquids allows one to observe a nonlinearity of the dielectric polarization (P) on the field strength (E) dependence. There are two main molecular phenomena which may cause this nonlinearity. The first one concerns the systems in which the intermolecular interactions (dipole-dipole or hydrogen bonding, for example) lead to the formation of aggregates with compensated dipole moment. In the liquid state the entities of low polarity are in equilibrium with the other entities (of different polarity) and/or with the non-associated molecules (monomers). In strong electric field such equilibrium undergoes a shift in favor to a more polar species (or monomers). This "chemical effect" makes that the dielectric polarization of liquid increases more rapidly with an increase of field intensity, than in the linear case. The nonlinear "chemical effect" measured with a weak alternating field E(w) shows a relaxation in a frequency region dependent on the rate of molecular aggregation process.

Here we discuss the second main phenomenon causing a nonlinearity of the P(E) dependence i.e. *the Langevin saturation of the dipoles orientation* in strong electric fields. This phenomenon leads to a decrease in permittivity of liquids. The nonlinear dielectric increment, defined as the difference between the permittivity value measured when strong electric field E_0 is applied to the dielectric (e_{E_0}) and when E_0 is not applied (e) : $\Delta\varepsilon_L = \varepsilon_{E_0} - \varepsilon$, is negative. For most liquids the De_L is proportional to the square of the biasing field strength E_0. The increment measured with an alternating field E(w) of small amplitude, shows a frequency dependence and can be presented in the complex form

$$\Delta\varepsilon^*_L(\omega) = \Delta\varepsilon'_L(\omega) - i\Delta\varepsilon''_L(\omega),$$

where De_L' and De_L" are the real and imaginary parts of the nonlinear dielectric increment, respectively.

We present the frequency dependence of the nonlinear dielectric effect caused by the Langevin dipolar saturation for the diluted benzene solutions of 4,4'-n-hexylcyanobiphenyl (6-CB) and 4-(trans-4'-n-hexylcyclohexyl)isothiocyanato-benzene (6-CHBT). The relaxation of the nonlinear dielectric increment induced by the coupling between the static electric field of high strength (10^7 V/m) and a field of small intensity and changeable frequency (1MHz - 3GHz) is interpreted with the Coffey theory [1].

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PHONON CONTRIBUTION TO ELECTROOPTICS COEFFICIENTS IN DOPED LNB SINGLE CRYSTALS

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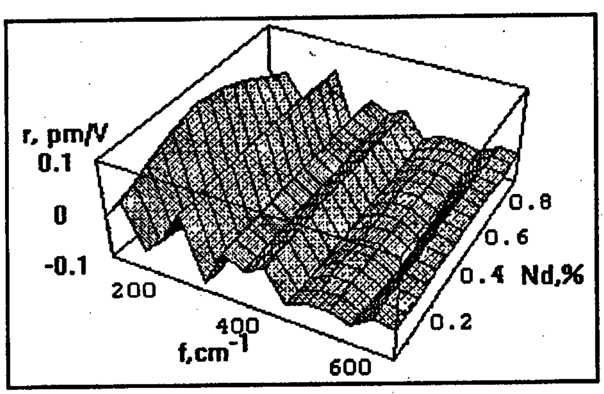
A new method of calculations of the eleectrooptics coefficient was proposed for LNB single crystals doped with Mg0 and Nd. Our approach is based on molecular dynamicssimulations and quantum chemicai calculations. We have revealed that two types of local centres are possible corresponding to Mg_{Nb} and Nd_{Li}; defect centres. We have found that the contribution of the phonon modes essentially influences the total electrooptics coefficients. The inclusion of the electron-phonon perturbation has improved a general agreement between the calculated results and experimental data. The contributions of different phonon modes to the output r_{222} are presented in Figure depending on Nd content.



The calculated spectra clearly show a change of the electrooptics modes with increasing Nd concentration. Moreover, it should be noticed that these modes give different contributions to the effective electrooptics coefficient. Therefore, one can modify the electrooptics coefficient by simple changing the Nd concentration.

DENSITY OF STATES A CONFORMON IN THE DISORDER POLYMERIC CRYSTAL

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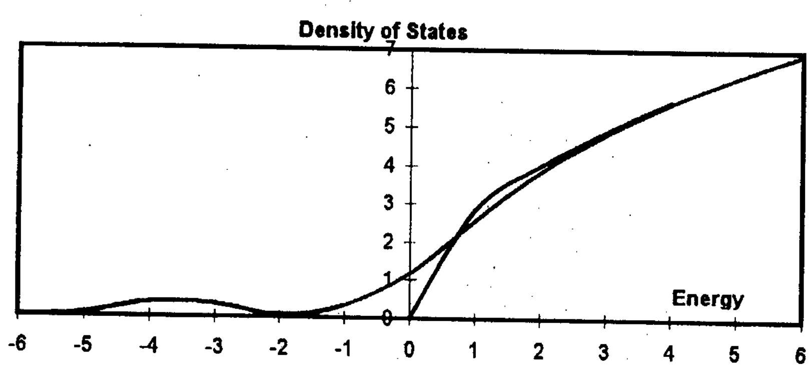
The conformon represents one of elementary excitations of a macromolecule, which dynamics determines properties of a conformationally disorder polymeric crystal. The important characteristic of a conformon is density of states, which account allows to analyse influence of structure on properties of a polymeric material (computer design of polymers). In conditions of the strong conformational disorder the numerical account of density of states of a conformon is carried out on the basis of model advanced in[1]. The Green's function of a conformon, law of a dispersion and effective mass is found. The analysis of influence of the allocated conformation of a macromolecule and conformational polymorphism on properties of conforma-



tional excitations in a macromolecular crystal is carried out.

On Fig. the qualitative dependence of density of states (in any units) for an electron in a zone of conductivity(E > 0) and in the forbidden zone (E < 0) is shown in view of conformational excitations of a macromolecular crystal.

This study was supported by ISSEP (Grant No.97-825d).

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THE INFLUENCE OF CONFORMATIONAL DEFECTS ON OPTICAL ABSORPTION IN A POLYSILANE

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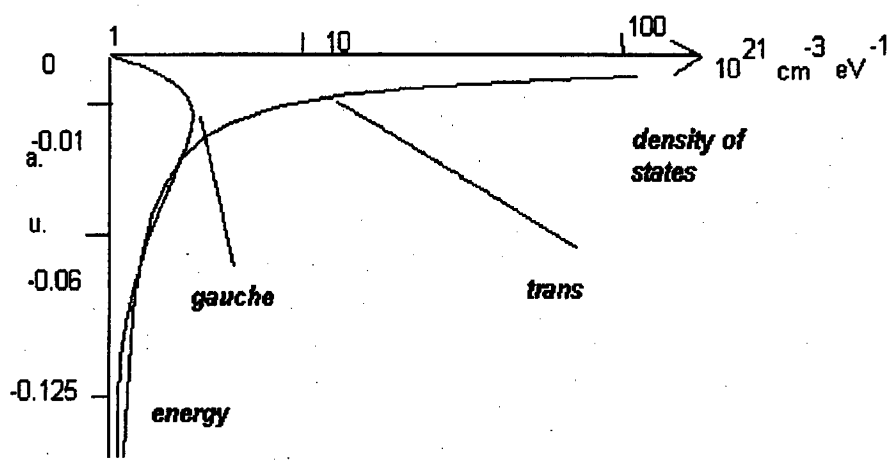
The polysilane is applied as a basis to reception of photoresistors, therefore factor of optical absorption is the important characteristic of polymer. The structure of a polysilane is characterized by model of casual spirals, for which the various conformational defects influencing optical properties of a polysilane and varying, in particular, density of electronic states in the forbidden zone are characteristic. In view of the data on electronic structure [1] and on the basis of model advanced in [2]



the accounts of density of electronic states of a polysilane for various conformations of a circuit forming structure of a macromolecular crystal were carried out.
On Fig. 1 density of states for a trans - conformation of a polysilane and for a conformation about a gauche - defect of structure is shown.
This study was supported by ISSEP (Grant No.97-825d).

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DIELECTRIC RELAXATION AND OPTICAL RESPONSE OF FLC SAMPLES IN FERROELECTRIC PHASE

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Dynamics of the FLC mixtures been studied using dielectric relaxa.tion and optical response in frequency domain. Measurements have been carried out for a number of SSFLC cells with different structures of FLC material. In the range of frequency extended from 10^{-2} to 10^{6} Hz at least 3 collective modes have been observed by both methods. Two collective processes in the low frequency region have been found. The first process of few hundreds Hz corresponds to the azimuthal reorientation of the director and is uniform over the boundaries and linear with the voltage. The relaxation time of this process weakly depends on the voltage, however shows a quadratic dependence with the thickness. The second process of the lower frequency corresponds to the domain reversed mode involving anchoring transition at the interfaces and is strongly non-linear with the voltage. At the lower voltage the process is initiated at defects on the boundaries and then domains grows over the sample. This switching usually goes through a sequence of steps between different states of the domains, and shows sometimes two peaks in the spectra. At the higher voltages the process is becoming uniform in the sample, however significant deformation of smectic layers may appear. Close to SC*- SA phase transition soft mode relaxation of the director is observed.

Simple computer model of the director orientation and dynamic in FLC cell following application square shape step or sinusoidal electric field has been successively employed. Both polar and dispersive coupling of the liquid crystal system to the surfaces have been considered in the model. From numerical solution of the set of dynamic equations, an azimuthal and polar angle profiles and their time evolution have been derived and compared with experimental results in time domain (optical response). For sinusoidal voltage the first harmonic contributions, real and imaginary part, have been derived from the model and then compared with optical response and dielectric relaxation spectra (in frequency domain). The model is able to reproduce both optical response and dielectric spectra.

DIELECTRIC RELAXATION OF THE IGEPAL IN 'THE PLANAR AND HOMEOTROPIC GEOMETRIES

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Dielectric relaxation measurements were carried out on the amphiphilic compound, igepal, in the wide frequency range 10^{-2} Hz – 10^{7} Hz as a funetion of temperature and voltage. Igepal is an amphiphilic liquid crystal with terminal O-H group. This compound can also form termotropic mesophases with extended networks of hydrogen bonds. Two dimensional proton conductivity along these networks can be expected. The measurements have been done for two geometries: planar and homeotropic of the LC cell. Strong relaxation peak is observed of the low frequency range (below 1 kHz). The frequency of the peak of about 100 Hz for planar sample can drop down to less then 1 Hz for well aligned homeotropic sample while the dielectric strength is inereasing by an order of magnitude. The relaxation spectra can be explained by the space charge polarisation related to electrolytic double layers.

DIELECTRIC RELAXATION IN CRYOPROTECTANTS

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The preservation of biological materials at low temperatures during a long time interval has many practical applications in medicine and biology, e.g. for successful cryo-preservation of whole organs for transplant surgery. In fact, it is well known that during the cycle of cooling to the temperatures of liquid nitrogen and heating back to physiological temperatures the cells are usually damaged. This damage is mainly originating from two distinct mechanisms, both due to ice crystallisation. The first mechanism is the osmotic dehydration of cells, due to increased concentration of NaCl solute, caused by pure ice crystallization in the extra-cellular liquid; the second is cell destruction through formation of intracellular ice, resulting in an increase of the intracellular solution volume. The main problem in cryobiology is thus to avoid both intracellular and extra-cellular ice crystallization. A solution to this problem would be the prevention of ice crystallization during cooling [1], facilitated by the addition to the biological systems of special materials known as *cryoprotectants*. The mechanism by which such agents act to reduce the damage caused by freezing and thawing is still a matter of continued investigation but is thought to involve, among other factors, the ability of these agents to cause an extensive development of metastable glassy phases, leading to a radical reduction of salt segregation. The methods conventionally used for the determination and the investigation of glass transitions or phase transformations in general, based on thermal analysis, are mainly Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) [2,3].

In this work, the contribution of the Thermally Stimulated Depolarization Currents (TSDC) method in the field of cryobiology, and more specifically in the study of the low frequency - low temperature dynamics of various biological sample-cryoprotectant complexes, is investigated. The important role of water in the recorded TSDC spectra has been shown by the application of TSDC techniques in a large number of hydrated biological materials [4-7]. More specifically, the above method provides a very sensitive tool for the detection of (a) dielectric relaxation mechanisms in ice originating separately from reorientation of free and loosely bound water, (b) relaxations directly related to glass transitions, associated with water tightly bound on the biomolecular surfaces which does not crystallize but seems instead to form a glassy state and (c) charge movements connected with dc-conductivity [8].

TSDC, TSPC (Thermally Stimulated Polarization Currents) and dc-conductivity measurements have been performed, in the temperature range from 100 to 300 K, on water solutions of $(CH_3)_2SO$ (dimethylsulfoxide or DMSO), a commonly used cryoprotective agent [9], in a wide range of DMSO concentrations. In a second stage the same techniques have been applied to the above solutions associated with protein albumin. Our study concludes with similar measurements using pig liver tissues (slices in thickness ~ 1mm) held in DMSO solutions of different concentrations. The obtained spectra were further experimentally analyzed in all cases using the 'thermal sampling' technique, which permits experimental decomposition of complex peaks in their simpler constituents and evaluation of activation energies.

Our results are discussed on the basis of free, loosely bound and tightly bound water molecules, freezable and non-freezable water, proton conductivity and glass transitions, as well as local and macroscopic motions [10] in the investigated systems, both from the physical and biological point of view. Finally, the possibility of using thermally stimulated currents techniques in cryobiology, as an alternative or complementary method to the more conventional thermal analysis methods, namely DSC and DTA, is examined.

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INVESTIGATIONS OF THE BIOPOLYMERS BY DIELECTRIC RELAXATION SPECTROSCOPY

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The water solution of β-Lactoglobuline, Agar-Agar and β-Lactoglobuline - Agar-Agar mixtures are investigated with Dielectric Relaxation Spectroscopy (DRS) in the frequency region 0,1 Hz - 1,6 GHz in frequency domain and time domain mode. A number of ways were tried to avoid ionic conductivity.

The dielectric relaxation properties of β-Lactoglobuline in water solutions and bonded water as well depends on concentration of the protein and temperature. The gelification process at the temperatures higher 50°C can also be characterized by the DRS.

The ways to study the complex biological systems in water solutions by the DRS is demonstrated on the example of β-Lactoglobuline - Agar-Agar systems. The technical particularities for the DRS method applied to water solutions of biopolymers are discussed.

NUMERICAL INVESTIGATIONS OF R.ELAXING FRACTAL SYSTEMS.

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It is widely known that most relaxing dielectric materials satisfy the *universal relaxation law*

$$-\frac{d\phi(t)}{dt} \propto \begin{cases} (\omega_p t)^{-n} & \text{for} \quad t \ll \dfrac{1}{\omega_p} \\ (\omega_p t)^{-m-1} & \text{for} \quad t \gg \dfrac{1}{\omega_p} \end{cases}$$

where $\phi(t)$ is the relaxation function, $0 < m, n < 1$ are material constants and ω_p is the characteristic relaxation rate of the system. Theoretical studies show that this type of response is exhibited by systems with fractal structure.

In the presented work we propose a relaxation model based on the parallel channel relaxation mechanism on fractals. We perform some numerical investigations which give a deeper insight into the model. We show how to sirnulate the fractal structure of the system by choosing a long tailed cluster size distribution. We also discuss the relationship between this distribution and the distribution of the relaxation rate of the cluster and express the necessary conditions for the special cases described by the empirical fitting functions such as Kohlrausch-Williams-Watts, Cole-Cole, and Cole-Davidson response functions.

A CONTINUOUS TIME RANDOM WALK MODEL OF THE LOW FREQUENCY DISPERSION PHENOMENON IN TISSUE.

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In this paper we present a new mathematical model of the tissue dielectric response in the least recognized region of dispersion α, which is related to the phenomenon known as anomalous low frequency dispersion (LFD).The dispersion α is one of four distinct regions in the typical dielectric response of tissue i.e.: diffusion, dispersion α, dispersion β, dispersion γ. The dispersion α takes place between 1 to 10^4 Hz and is attributed to various reasons: interfacial phenomena, counter-ion relaxation associated with intrinsic membrane charges, ion transport across membranes, and ion transport around spherical membrane structures. It is characterized by two fractional power laws in frequency with an overlap at the characteristic crossover frequency $\omega_c \approx 10^3$ Hz.

$$\chi'(\omega) \propto \chi''(\omega) \propto \begin{cases} \omega^{-n} \text{ for } \omega << \omega_c \\ \omega^{-m} \text{ for } \omega >> \omega_c \end{cases} \qquad (1)$$

where $0.85<n<1$, $0<m<0.2$.

A number of experimental studies have been made to investigate the conduction pathways in the tissue. There was discovered an existence of lateral hopping charge transport along membrane-electrolyte interfaces of the tissue. It has been proposed that either water molecules from the tissue fluid are hydrogen bonded to the lipid head groups of membranes, which constitutes a proton conducting network, or protons hop along the surface of the membranes between ionizable groups of protein molecules where they are trapped by the electrostatic attraction. This hopping conduction may explain why the properties of the region α in the tissue dielectric response resemble very much another phenomenon, discovered in non-biological dielectrics, which is referred to as "low frequency dispersion" (LFD). It can be observed in systems dominated by hopping conduction. In the hopping conduction, called trapping, a charge is transported via a sequence of steps from one randomly located site to another, by the applied electric field. Since the frequency characteristics (1) of dielectric materials may be easily transformed, by means of Fourier transform, into the time domain, we analyze the time domain response function, whose physical significance is the electrical discharge current, which can be detected in the circuit of the relaxing material, formerly polarized by a step-function voltage. The time domain analysis allows us to employ in a natural way the random walk approach to model the dielectric response of tissue in the range of the dispersion α.

The continuous time random walk (CTRW), a walk with random waiting times T_i between successive random jumps R_i, was introduced into statistical physics by Montroll and Weiss in 1965. Since then it has been studied extensively and applied to explain dynamical properties of disordered systems. It has been found that many important features of relaxation and transport in disordered systems can be attributed to the long-tailed waiting time distributions. Here, we present an approach to the CTRW which is based directly on the analysis of the the distance reached up to large t by particle initially at the origin, which is a cumulative stochastic process defined as a sum of random number N_t of random jumps R_i:

$$R(t) = \sum_{i=0}^{N_t} R_i \qquad (2)$$

where $N_t = \max\{k: \sum_{i=0}^{k} T_i \leq t\}$, $R_0 \equiv 0$, $T_0 \equiv 0$. $\{R_i\}_{i>0}$ is a sequence of independent, identically distributed (iid) random variables representing jumps, and T_i is a sequence of positive iid random variables representing waiting times. By applying the limit theorems of probability theory the explicit forms of the asymptotic random variable $R(t)$ in the one-dimensional CTRW can be derived. The results allow one to establish easily the expected position of the walking particle as a function of time and consequently to find its average velocity and, therefore, the relaxation current.

We show that the form of LFD phenomenon may be rigorously attributed to the self-similar character of hopping transport. A great diversity of trapping times and fractal properties of ion jumps account for two power-law regions. These properties were expressed by means of random variables from the stable domain of attraction. We have obtained that the trapping time of ion can be represented by a random variable from the domain of attraction of the completely asymmetric stable variable S_λ, $0<\lambda<1$, with infinite expected value. The parameter λ of the waiting time distribution determines the high-frequency power law exponent $m=\lambda$. Similarly, the length of jumps can be expressed by a random variable from the Gaussian domain of attraction (i.e. with a finite variance) for the high frequency $\omega >> \omega_c$ region, and asymmetric stable variable S_γ, $0<\gamma<1$, with infinite expected value for the low frequency $\omega << \omega_c$ region. The parameter γ of the distribution of jumps, jointly with the waiting time distribution parameter λ, determines the low-frequency power law exponent $n = \lambda/\gamma$.

DETECTION OF STRUCTURAL INHOMOGENEITY IN GRADED INDEX POLYMER MATERIALS BY SPACE CHARGE MEASUREMENTS: NUMERICAL SOLUTIONS

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An increasing attention has been paid to graded index (GI) polymer materials due to their very interesting physical properties. Recently, a number of applications of GI polymer materials for optical purposes have been reported [1,2], In case of so-called axial G1 media the index of refraction varies continuously along the optical axis but the index values remains constant on the planes perpendicular to the optical axis. The idea of producing of gradient polymers was first presented by Shen and Bever [3]. The method most frequently used to obtain GI polymer materials is by diffusion of guest monomer into a polymer gel substrate. It has been shown that the gradient profile of the guest polymer need not be consistent with the profile resulting from Fick's law. This means that an independent method of determination of the gradient profile might be useful.

Guest (or impurity) molecules in a host molecular solids form local states (traps) both for charge carriers and excitons [4, 5, 6, 7, 8]. The depth of electron traps due to impurity molecules is given by [4]:

$$E_t^e = (A_G)_{guest} - (A_G)_{host} \qquad (1)$$

where A_G is the electron affinity. If $E_t^e > 0$ the electron trap is formed, for $E_t^e < 0$ we have to do with the electron antitrap. The depth of local states for holes is given by the difference of ionization energies of the guest and host molecules respectively.

If the guest molecules possess a permanent dipole moment the energy of the trapping level changes due to the additional charge-permanent dipole interaction [7,8]. It has been shown that the trap depth due to charge-permanent dipole interaction is equal to about 0.1 eV for the dipole moments between 3-4 D [9,10].

Taking into account the above remarks it may be supposed that the polar polymer gives rise to electronic states in the graded index material. The concentration of the states depends on the concentration of the guest molecules. However, the values of the two concentration need not be the same, as one trapping state may be formed by a few guest molecules forming dipole cluster [11].

As it was mentioned above, the gradient profile of guest molecules may be not consistent with the Fick's law which means that an independent method of determination of the concentration of guest molecules is required. In order to determine the concentration from space charge (SC) measurements one not only must be able to determine the spatial trap distribution but one also must know the relation between the concentration of guest molecules and the concentration of traps to which the guest molecules give rise. The present contribution concerns the first part of the problem.

It is shown that stationary SC limited currents may lead to determination of spatial distribution of traps at the injecting electrode.

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SPACE CHARGE LIMITED CURRENTS FOR THE CASE OF TRAP INDUCED DEFECT GENERATION

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Space charge limited currents are investigated far the case when energy released during carrier capture by kra.ps is revealed to the formation of defectimpurity complexes. A model of semiconductor with deep acceptor traps for electrons (N_t)is considered. As a result of the influence of the energy defectimpurity complexes of type negatively charged acceptor ~ positively charged interstitial in n-semiconductors or positively charged donor - negatively charged vacancy in p-semiconductors) are formed. It is shown that emission of electrons from the defectimpurity complexes will change in comparison with usual one (i.e. from single simple acceptor center). Consequently, occupancy of the defect-impurity complexe with electrons will change in comparison with that of single simple trap and its fill factor has the form:

$$f_t = \frac{n}{n(1+\alpha n)+n_1} \qquad (1)$$

where $\alpha=\eta\ (g/r)C_nN_t$- the coefficient, describing the processes of defectimpurity complex formation and emission of electrons from the ones; ,g and r are the coefficients describing generation and decay of defect-impurity complexes; C_n, - is the capture coefficient of electrons by a single simple trap η describes variation of the capture coefficient due to generation of defectimpurity complexes; n_1 is the statistical factor of Shockley-Read for the trap level.

Consequently classic Lampert .taw for space charge limited currents will change too

$$J = \frac{9}{8}\frac{\mu n V^2}{\left[1+\left(\frac{N_t}{n_1}\right)\cdot(1+\alpha n_1)\right]d^3} \qquad (2)$$

where d is the sample thickness.

Concentration of traps N_t determined from (2) considerably decreases (αn_1 times) compared with the usual one. That permits to explain distinction ($10^2 \div 10^5$ order of magnitude more) between traps concentration N_t determined from usual Lampert's law and all other experimental methods (particularity DLTS method) that always takes place.

RELATION BETWEEN STRUCTURE AND DIELECTRIC PROPERTIES OF HYDROGELS

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The dielectric response have been studied within the wide region of frequencies (20Hz-10MHz) and temperatures (290-350 K) for dried hydrogeles based on Poly(Methacrylic Acid, Sodium Sode) (PMAS). Hydrogeles have been prepared with different monomer concentration (20, 30 and 40%) during polymerisation. Also corresponidng hydrogels were polymerised, adding rodamine.

As a result of experiments rather high values of dielectric constant appeared (100-500), that increased according to the values of concentrations. Such high values are, probably, connected with water, held in place with the polymer net, and condition of remained water is determined by the structure of the three-dimentional polymer. Water effect was also investigated by adding water to the dried gels.

Change in dtelectric properties after adding of rodamine was observed. Change in conductivity meehanisms of PMAS is, probably, connected with appearance of rodaminė polar groups in the structure of hydrogels.

TRAPPING AND RECOMBINATION KINETICS IN SPATIALLY CORRELATED SYSTEMS

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Physical parameters of trap states are investigated by a variety of methods. Many of them are based on the observation of thermally stimulated relaxation spectra. Among them, thermoluminescence (TL) and Thermally Stimulated Conductivity (TSC) phenomena are one of the basic tools. A series of peaks appearing on TL or TSC spectrum may be attributed to trap levels having different activation energies E_i. Theoretical description of these non-equilibrium phenomena usually assumes uniform distribution of traps and recombination centres [1,2]. Another extreme case was the model of localised transitions by Halperin and Braner [3] regarding hole-electron pairs trapped close to each other. Only for the two cases it was possible to formulate differential equations describing charge carriers' kinetics.

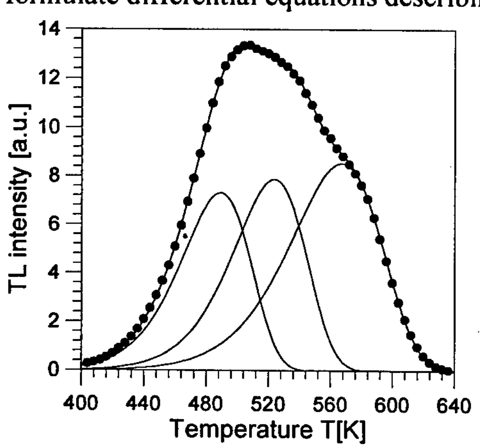

Fig. 1. Results of glow curve deconvolution performed for a single 'spatially correlated' TL peak calculated for E=0.9 eV, ω=0, ρ=0.33 and r=1000. The spectrum can be perfectly deconvoluted for three first-order peaks (b=1) having 'energies' E_1=0.893 eV, E_2=0.911 eV and E_3=0.932 eV.

Using recently developed Monte Carlo technique the kinetics of trapping and recombination may be studied in systems with different kind of spatial correlation between traps and recombination centres [4]. This allows to study a variety of cases much closer the reality. In some situations the spatial correlation comes as a consequence of a structure of a solid - e.g. in polycrystalline samples. However, one can expect similar distribution in every case, where a sample (semiconductor or insulator) is exposed to a high-energy radiation, which produces large defects - traps and recombination centres, most probably assembled into groups [5]. The later case is especially important due to dosimetric applications of TL.

In this paper we present new features of TSC and TL spectra simulated numerically for different types of spatial correlation. Calculations presented here clearly shows the importance of spatial correlation effects in the analysis of charge carriers' relaxation kinetics. Unquestionably, the basic analytical models for the non-equilibrium trapping and recombination kinetics, though mathematically quite complex, do not cover the variety of all physically admissible cases. For some typical trap parameters, in the presence of spatial correlation, TL and TSC curves reveal unusual properties that cannot be described in terms of standard models. Typical example is presented in fig. 1. The TL spectrum was calculated in the framework of 'spatial correlation' model assuming one monoenergetic trap level E=0.9 eV, retrapping coefficient r=10^3 and low concentration of deep traps $\omega \equiv M/N << 1$. Spatial correlation is characterised by the parameter $\rho = 1/\overline{N}$, where $\overline{N}$ is the number of traps of the same kind in a single group. The single TL spectrum appears to consist of three individual peaks. Applying well known curve fitting techniques one can easily 'deconvolute' the spectrum for three first-order peaks with different activation energies. Although mathematically correct, this method of analysis has no physical sense.

The results of extensive numerical simulations indicate that the effects of spatial correlation play important role especially in systems characterised by high retrapping coefficients and low concentrations of deep traps. In systems consisting of a few discrete trap levels high values of the retrapping coefficient r make difficult analysis of thermally stimulated relaxation spectra for closely situated energy levels because two individual peaks appear to be a single one. Surprisingly, strong spatial correlation increases resolution of TL and TSC measurements. It allows to identify closely situated energy levels even for systems with very high retrapping. Nevertheless, theoretical analysis of these intermediate cases $(0 < \rho < 1)$ is complex. The range of applicability of some standard methods developed for the analysis of TL and TSC is discussed. A special attention is paid to classical deconvolution techniques and initial rise methods.

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MOLECULAR MOTIONS IN PVDF : A COMBINED THERMOSTIMULATED CURRENT AND DIELECTRIC RELAXATION STUDY

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The correlation between Dielectric Spectroscopy (DS) in frequency domain and ThermoStimulated Current (TSC) is actually a subject of interest. Indeed, with the increase of powerful analyses, a comparative study of these two dielectric techniques can be undertaken. For this purpose, a semi-crystalline polymer, Poly(VinyliDene Fluoride) in a form (a-PVDF) has been chosen as model.

On the one hand, a dielectric study in frequency domain has been performed in a wide frequency range [10^{-2}, 10^{7} Hz] using a Dielectric BroadBand Novocontrol Spectrometer. The classical isothermal procedure is carried out as temperature swept the -80 to 80°C range by step of 5°C. The dielectric relaxation map, shown in a 3D plot, displays three relaxations in order of increasing temperatures : g, b_{lower} and b_{upper} attributed to the dielectric manifestation of the secondary relaxation and dielectric manifestation of the lower and upper glass transitions respectively.

On the other hand, a low frequency analysis has been carried out by ThermoStimulated Current (TSC). As in frequency domain the g, b_{lower} and b_{upper} processes, assigned to the secondary relaxation and to the manifestation of lower and upper glass transition,respectively, have been observed by TSC. In addition, a broad and intense symmetric peak was recorded and attributed to the a_c process often observed in semi-crystalline polymers.

Firstly, a comparative analysis has been performed on these complex spectra. The DS relaxation spectra have been analysed by a sum of Havriliak Negami functions in order to extract relaxation times by subtracting the influence of the direct conductivity effect at high temperature. Indeed, in the lower frequency side of the e"(w) peak of the b_{upper} process the conductivity influence was significant. The obtained relaxation times were plotted on an Arrhenius diagram. The relaxation time of the b_{lower} follows a Vogel - Fulcher - Tammann (VFT) law whereas for the g and b_{upper} processes, the relaxation

time obeys an Arrhenius law. Owing to the obtained laws, an extrapolation of these modes to the equivalent frequency of the TSC, f_{eq} about 10^{-3} Hz, showed the good agreement between complex spectra of these two techniques.
The obtained spectra are well known to be complex, their logarithm half width being greater than 1.14 which would be expected from a Debye process. So, according to the superposition principle of Boltzmann, we assumed the existence of a distribution of elementary Debye processes, opering in parallel, which are constitutive of the complex response.
Recently, several numerical methods have been developed in order to determine the distribution function of relaxation times from DS data. From all these methods Tikhonov regularization is the best-known one to resolve the Fredholm integral equations of the first kind as encountered in DS [1]. To obtain physical solution of this ill-posed problem, the Self Consistent method (SC) of Honnerkamp and Weese [2] has been used. Thus, distribution functions of relaxation times have been determined in the [-80, 80°C] temperature range.
On the other hand, to resolve complex TSC spectra into elementary Debye processes, an experimental method has been proposed this last decade. This method labelled Fractional Polarisation (FP) is a powerful experimental procedure which gives access to the fine structure of the material's relaxations in a wide temperature range. This method is based on a sampling of the complex spectrum into elementary spectra. As in frequency domain, elementary spectra were analysed as Debye processes and a set of elementary relaxation times was obtained.
The shifts with temperature of relaxation times obtained from both DS analysis and FP experimental method were compared in an Arrhenius diagram and evidenced a good agreement between the two techniques. Furthermore the comparison of activation enthalpies emphasised the complementarity of both dielectric spectroscopies.

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ANALYSIS OF THE NONLINEAR CIRCUITS WITH FERROELECTRIC CAPACITOR IN THE FR.AME OF LANDAU-DEVONSHIRE THEORY

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1. Introduction

The nonlinear properties of ferroelectric ceramic capacitors used in circuits are much influeneed by various parameters: temperature, amplitude, frequency and shape of input signals. A large number of authors tried to describe the nonlinear properties using adequate analytical functions, bascd on the Miller model [1-2]. A better physical description of the ferroelectric can be developed in the frame of Landau-Devonshire theory [3]. We used this approach in the present paper to characterise the hysteresis loop of the ferroelectric material. A polynomial dependence for E(P) was employed for fitting the experimental hysteresis and to find the Landau-Devonshire coefficients.

2. Experiment

We studied ferroelectric ceramic capacitors made of barium titanate ceramics with average grain size of 20μm, thickness d=0.34 mm, with silver electrodes having area $S=30.25mm^2$. A Sawyer-Tower circuit with a computer controlled oscilloscope was used for recording the P(E) hysteresis loops.

3. Results

Knowing the Landau-Devonshire coefficients, we theoretically described the ferroelectric response under different input signals, in various RC, CC and RLC circuits. The simulated dependencies are in good agreement with those obtained experimentally.

4. Conclusions

A method for solving the nonlinear differential equation of circuits containing ferroelectric capacitor was developed using the Landau-Devonshire theory. We used the P(E) hysteresis loops for a polynomial fitting in order to obtain the model parameters. With these parameters, we simulated other nonlinear responses in RC, CC and RLC circuits containing the ferroelectric capacitor, under various conditions. More complicated circuits and input signals can be described using this method.

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GRAIN SIZE DEPENDENCE OF THE DIELECTRIC PROPERTIES IN BARIUM TITANATE CERAMICS

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1. Introduction

Grain size effects on barium titanate ceramics were investigated by several authors, using various techniques [1-2]. They reported a decrease of the Curie temperature with decreasing the grain size of barium titanate ceramics, and a maximum of the dielectric constant at a critical size of about 1 μm [3]. In the present study, we analysed the grain size effect on the dielectric constant in barium titanate ceramics with average grain sizes between 0.5μm and 20μm, at various frequencies.

2. Experiment

The experiments in this work were performed on barium titanate ceramic samples having four average grain sizes: 0.5μm (A), 2.5μm (B), 10μm (C) and 20μm (D). The grain sizes were estimated using atomic force microscopy (AFM) images of as-sintered surfaces. The dielectric constant was measured during the phase transition with a bridge HP 4284 LCR Precision Meter at various frequencies between 20 Hz - 1 MHz.

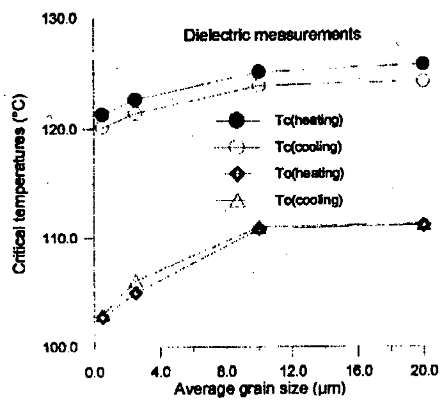

Fig. 1 Grain size dependence of the transition temperatures.

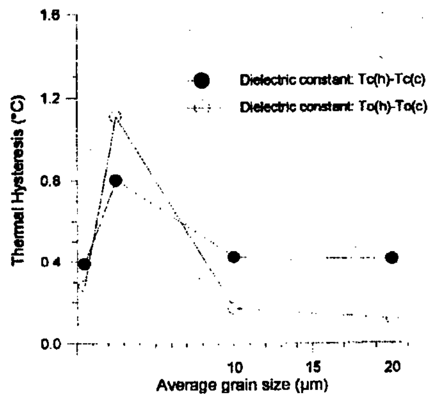

Fig. 1 Grain size dependence of the thermal hysteresis.

3. Results and discussion

The ferroelectric-to-paraelectric phase transition was investigated by recording the dielectric constant, on a heating/cooling cycle. The Curie temperatures decrease with decreasing the grain size, from 125°C to 120°C and the Curie-Weiss temperatures from 1 10°C to 102°C (Fig. 1). All the samples show thermal hysteresis, defined as the difference between the critical temperatures on heating and cooling. The thermal hysteresis is grain size dependent (Fig. 2) and shows a maximum value for the sample B.

The real part of the dielectric constant decreases monotonous with the frequency in the range 20 Hz-1 MHz (Fig. 3). Our ceramics show appreciable dispersion which appears as size dependent in the fi-equency range of (0.25-1) MHz (Fig. 4), with a maximum of the imaginary part of the dielectric constant for sample t3. Since the single-domain crystals of barium titanate exhibit a dispersion only for greater frequencies (10^{10}-10^{11}Hz), the observed behaviour is related to the particle sizes which in turn affect the type and the density of domain walls in the ceramic samples.

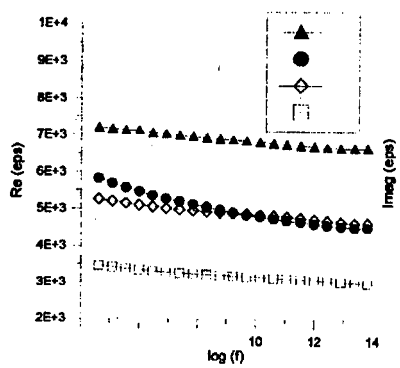

Fig. 3 The frequency dependence of the real part of the dielectric constant.

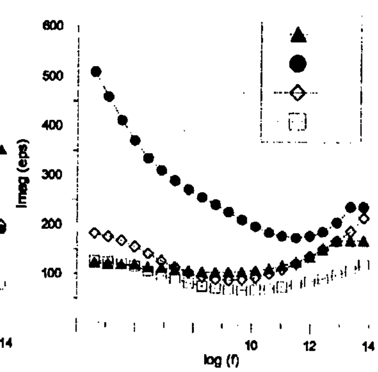

Fig. 4 The frequency dependence of the imaginary part of the dielectric constant.

4. Conclusion

We believe that the peculiar behaviour of ceramic B of 2.5 μm observed in the dielectric measurements, i.e maximum value for the thermal hysteresis and the dispersion in low frequency range (0.25-1)MHz is due to the distribution of grain sizes in the range including the critical size of 1 μm, where the density of 90° walls is maximum [3]. All the physical properties of barium titanate ceramics exhibit important variations in this interval of grain size. To elucidate this effect, a new series of dielectric measurements are necessary, for frequencies greater than 1 GHz.

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DIELECTRIC RELAXATION PHENOMENA IN SIDE CHAIN LIQUID CRYSTALLINE POLYCARBOSILANE OF VARIOUS SPACER LENGTHS

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Side chain liquid crystalline polycarbosilanes were synthesized in the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences (Łódź). Their thermodynamic parameters and kinetics of mesophase formation were analyzed elsewhere[1]. A different mesophase structure was reached by the variation of the number of alkyl spacer groups from x=3 (no mesophase), x=4 (nematic mesophase) to x=11 (smectic mesophase). A major location for permanent electric dipoles in the liquid crystalline polymers are mesogenic groups which have effective dipole moment. The present work is concerned with dynamic dielectric relaxation phenomena of polymers at frequency ranging from 10^{-2} to 10^{6} Hz as a function of temperature up to isotropic phase. Three relaxation transitions known as β, α and δ were found. Their position and intensity appeared to be strongly dependent on the spacer length (Fig. 1).

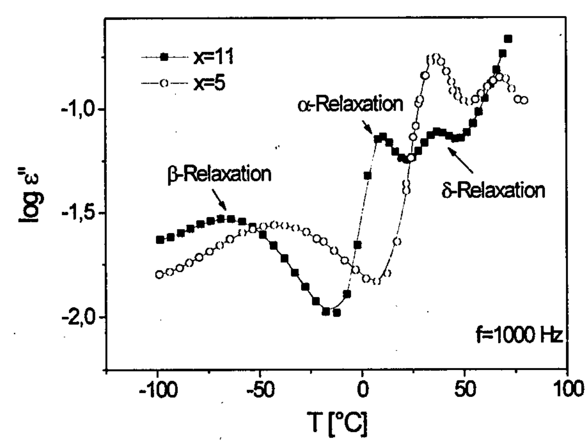
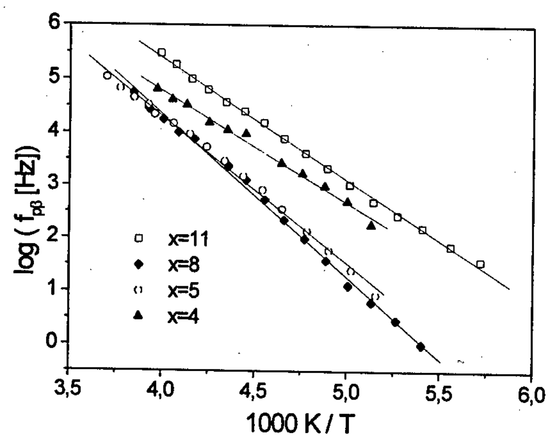


Fig 1. Dielectric relaxation spectra of liquid crystalline polycarbosilanes x - spacer length.

At low temperatures β relaxation takes place which corresponds to fluctuational dynamics of a transverse component of dipole moment. The characteristic relaxation rate of β relaxation has Arrhenius-like character (Fig. 2). At medium temperature α relaxation is observed which is considered as a dynamic glass transition. At higher temperature δ relaxation is related to the dynamics of longitudinal component of dipole moment.



Fig'2. Temperature dependence (fitting to Arrhenius equation) of the relaxation rates for β relaxation.

The dependence of the activation energy of the relaxations on spacer length is found and discussed.
The effect of spacer length in the main chain liquid crystalline polyesters was also observed[2, 3].

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TRANSPORT PROPERTIES OF GLASSY AND CRYSTALLIZED Bi-Sr-Ca-Cu-O SYSTEM

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It has been found that glasses in the system Bi-Sr-Ca-Cu-O are eonverted into high-T_c superconductors after proper annealing [1]. During annealing a different crystalline ghases grow in the glass matrix that create some granular structure with metallic (or superconductive) and insulatulg regions. When the concentration of metal is small, the metals forms small isolated grains embedded in an insulating matrix and conductivity is activated. This generally called the dielectric regime. As the proportion of metallic phase is increased, the grains become larger, the activation energy falls and; when conaeeted metallic pathways through the sample are established, the system undergoes a metal-insulator transition to a metallic state.

The present paper reports the results of DC conductivity measurements in $Bi_4Sr_3Ca_3Cu_4O_x$ glass and crystallized glasses with different concentration of Bi_2Sr_2CuO metallic phase (2201 superconducting phase below 20K) in dielectric regime.

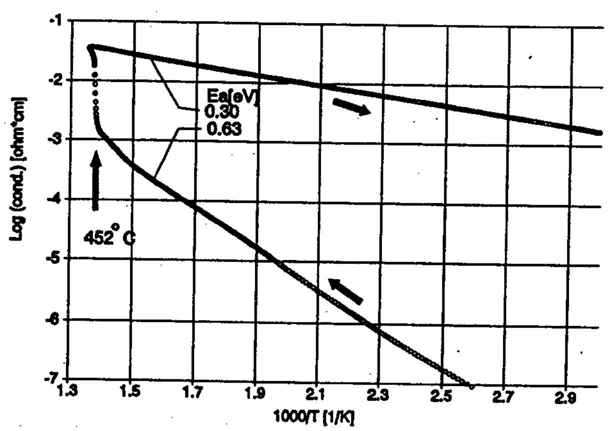

Fig. 1 Temperature dependence of conductivity and crystallization effect in $Bi_4Sr_3Ca_3Cu_4O_x$ glass.

In glassy state the DC conductivity has been measured in the temperature range between 100-725 K. The small polaron hopping between copper ions in a different valency state Cu^{1+}–Cu^{2+} is found to be the most appropriate conduction mechanism in this glass [2]. A sharp increase in the eonductivity is observed at 452°C, which agree fairly well with tlie temperature of crystallization of 2201 superconducting phase (Fig. 1). The mean sizes of 2201 crystalline grain were evaluated from the broadening of XRD peaks. The mechanism of electrical conductivity in crystallized glasses can be explained as a result discontinuous metallic structures of 2201 phase which appear in the glass matrix during anealling. For these samples, DC conductivity wore measured from 5 K to the room temperature (Fig.2). The conductivity exhibit $T^{-1/2}$ dependence between 4 K and 40 K and $T^{-1/4}$ dependence above 40 K. This change is explained as a consequence of occurrence of the Coulomb gap resulting from long-range Coulomb interaction between grains [3]. Additional mechanism that also leads to $T^{-1/2}$ dependence of conductivity is attributed to superconductivity effect below superconducting transition temperature of the 2201 phase. In this case the reduced charge transfer rate is caused by the superconducting gap opening in the grains [4].

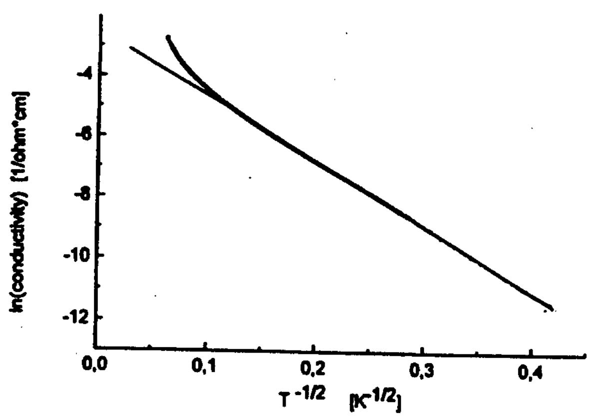

Fig. 2 Conductivity vs $T^{-1/2}$ for $Bi_4Sr_3Ca_3Cu_4O_x$ glass after annealing at 472°C for 310h.

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PHYSICAL PROPERTIES OF THIN EVAPORATED FILMS OF INDANDIONE–1,3 PYRIDINIUM BETAINE AND IT DERIVATIVES

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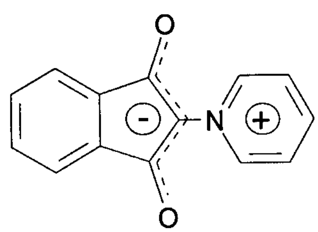

IPB

Indandione-1,3 pyridinium betaine (***IPB***) compound and it derivatives belongs to the series of highly polar intramolecular salts in which the cation and anion part are covalently bounded in one molecule. The strong interaction between donor and acceptor components of ***IPB*** molecule is observed and partial intramolecular charge carrier transfer from indandione anion to the pyridinium cation takes place in the ground state, similarly to the case of strong intramolecular DA complexes or in ion radical salts.

Crystals and vacuum evaporated films of ***IPB*** and it derivatives show a number of unique physical properties: due to optically induced charge in the sign of the electric dipole moments of the ***IPB*** molecule the possible optoelectrical effects and the non-linear optical effects were observed; the reversible photo and electro-refrigence effects also have been observed; evaporated thin films may be regarded as excellent photo-conductors. The quantum efficiency of photoconductivity β is electric field dependent and reaches the values of β=0.2-0.85 electron/photon at $E \geq 10^4$ V/cm. At higher electric fields $E \geq 10^5$ V/cm field enhanced photoconductivity has been observed, reaching the values of $\beta = 10^2$ electron/photon.

In this work, in order to study influence of heteroatoms and different functional groups in molecule on electronic properties, the wide class of ***IPB*** derivatives are chosen.The experimental data of electronic structure of thin evaporated films of ***IPB*** and it eleven derivatives are described.

It is shown that the vacuum evaporated films of ***IPB*** and it derivatives are of polycrystalline structure. The crystallites increased by increasing the thickness of organic layers. From experimental data obtained by scanning microscope follows that in the evaporated ***IPB*** films with thickness L=0.2μm the sizes of crystallites are 0.2x0.65μm, but in the film with L=1.35μm, the crystallites are 1.0x0.7μm.

IPB and it derivatives are insulators in the dark and conductivity σ is in the range from $\sigma=1x10^{-16}$ S/cm to $\rho=1x10^{-13}$ S/cm, which is typical for single component organic materials.

As follow from space charge limited current (SCLC) and thermally modulated space charge limited current (TM-SCLC) experimental data only the very shallow sets of hole traps close to conductivity level are obtained for ***IPB*** and it derivatives. The total density of given set of traps N_t are in the range $N_t=1x10^{14}-10^{17}$ traps/cm^3. It has been established, that the value of total density of traps N_t is influenced by the crystalline structure of the organic layers,i.e., the N_t of shallow traps decreased with increasing sizes of crystallites.

IPB and it derivatives possess a large permanent dipole moments and high molecular polarizability leading to low adiabatic energy gap E_G^{Ad} values. In the case of ***IPB*** thin films the adiabatic energy gap is of $E_G^{Ad}=2.35$eV. The presence of heteroatoms in the indandione part of molecule decreases the value of energy gap E_G^{Ad}. The substituting of oxygen atom in the indandione part of molecule by sulphur atom is followed by decreasing of the values of E_G^{Ad} by 0.25eV. In the case of substituting both oxygen atoms by sulphur atoms, the difference of the values of E_G^{Ad} is more important, i.e. about 0.63eV and reaches value $E_G^{Ad}=1.72$eV. Whereas the substituting of pyridinium part of molecule to derivatives of 2-(1,3-dithiolan-2-ylidene) causes the increase of the value of E_G^{Ad} by 0.15-0.35eV.

The basic energy parameters of compounds such as adiabatic energy gap E_G^{Ad} should be the same both for crystal and vacuum evaporated thin films. The presence of different heteroatoms and functional groups in a molecule might influence the basic parameters of energy structure of crystals, but structural changes are mostly might influence the energy parameters and total density of local trapping states.

IPB and its derivatives belongs to the class of photosensitive molecular crystals. By irradiation with visible light at ohmic region the current increases by several orders of magnitude.

The quantum efficiency of photoconductivity $\beta(h\nu)$ in visible spectral region at 2.1-2.7eV are in the range from $1x10^{-4}$ to 0.1 el/photon. The quantum efficiency of photoconductivity β for ***IPB*** thin film is electric field dependent and reaches the values of the order of $\beta=0.2-0.85$ electron/photon at $E\geq10^4$ V/cm. At higher electric fields $E\geq10^5$ V/cm field enhanced photoconductivity has been observed, reaching the values of $\beta=10^2$ electron/photon.

DIELECTRIC PROPERTIES OF BAGASSE AND ITS CONSTITUENTS

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Dielectric properties of bagasse raw material and its constituents, cellulose and lignin was studied. The effect of γ- radiation of different doses (0 - 40 M.rad) on the dielectric properties of these investigated samples was also studied. However, the study of the grafting process of these materials with acrylamide using γ -radiation (dose 20 Mrad)was also clarified. The dielectric properties of these grafted materials were also investigated.

ELECTROOPTICAL EFFECT IN PDLC COMPLEX SYSTEM PREPARED BY SOLUTION CAST METHOD

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The main aim of this study was to present reorientation processes induced by external fields in liquid crystal-polymer systems. To consider applicability of these materials in optoelectronics it is very important to understand factors which determine the type and range of ordering and measurement of electrooptical parameters.

Thin PDLC layers which contain dispersed droplets of liquid crystal in the polymer matrix are formed as a result of forced separation of phases from a homogeneous solution of liquid crystal and polymer. Various phase separation techniques are known[1-5]. In these investigations polymer layers which contain liquid crystal (W-52) dispersed in polycarbonate (PC) were obtained by forced separation of components in the course of rapid solvent evaporation (methylene chloride). The PDLC systems contained various weight fractions of liquid crystal (from 20% to 60%). Complete phase separation took place at room temperature (investigation of the dependence of polarized light transmission on time) after 30 minutes of evaporation of highly volatile methylene chloride.

The PDLC systems of a known morphological structure (microscope, image analysis) were subjected to thermo- and electrooptical tests and DSC analysis.

On the basis of DSC and TOA analysis it was found that with an increase of liquid crystal concentration in the sample the value of T_g of the PC matrix decreased. Taking into account the measurement of the heat of isotropization of liquid crystal it was found that about 80% of liquid crystal remains dissolved in the polymer which caused a significant drop of PC glass transition temperature. About 20% of liquid crystal was precipitated in the form of droplets. The isotropization temperature of liquid crystal in the sample did not change remarkably depending on its percentage in the polymer which is a good evidence of liquid crystal purity in the droplets.

The electrooptical studies show that only PDLC samples with initial content of liquid crystal exceeding 40% have good electrooptical properties.

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PYROELECTRICITY IN PVDF/PZT CERAMIC COMPOSITES OF 0-3 CONNECTIVITY

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The pyroelectric properties of *PVDF/PZT* composites with 0-3 connectivity pattern are studied experimentally. *PVDF/PZT* composites filtns have been produced by introducing fme grain *PZT* powder in the matrix of *PVDF* using a well-known hotpressure method. These films were polarized in a strong **DC** electric field at elevated temperatures. The pyroelectric coefficient of *PVDF/PZT* depends on the volume fraction *PZT* in composite, on the electric field strength and temperature. The results of measurements of the pyroelectric properties of the *PVDF/PZT* mixture with the various volume fraction of the components are given in this report.

INFRARED SPECTROSCOPY OF PLZT THIN FILMS

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We have investigated several thin films of (Pb_{1-x} La_x)(Zr_y Ti_{1-y})O_3(PLZT 100(x/y/1-y)) were deposited by sol-gel technique on sapphire substrates with composition 9.5/65/35, 8/65/35 and 2/95/5. Depending on the deposition conditions pure perovskite, pyrochlore and mixed perovskite-pyrochlore phases were obtained. The particular phases were found by x-ray diffraction. The infrared transmission spectra of the films were measured in the spectral range 10 - 250 cm^{-1} and in the temperature range 300 - 530 K. No phonon modes were seen below 250 cm^{-1} in the pyrochlore phase whereas the perovskite phase is characterized by strong phonon modes at 50-80 cm^{-1} and 210 cm^{-1} range. This gives a good ground for identification of the crystal phases which are in agreement with x-ray analysis. The most important deposition factor which determines the structure of thin films is the existence of a $PbTiO_3$ seeding layer. If the seeding layer is present the thin film prefers the perovskite structure. The vibration modes were assigned in agreement with bulk materials and in the case of 2/95/5 composition their temperature dependence was studied. In the perovskite thin films three vibration modes were observed below 360 K in the spectral range 20 - 250 cm^{-1}, which was limited by transparency of sapphire substrate. Above this temperature only two of the modes could be seen. The temperature of 360 K corresponds to the temperature of the phase transition into incommensurate phase which has been recently reported in the literature.

EFFECT OF TEMPERATURE AND TIME ON THE COMPLEX PERMITTIVITY OF AN INSULATING MATERIAL

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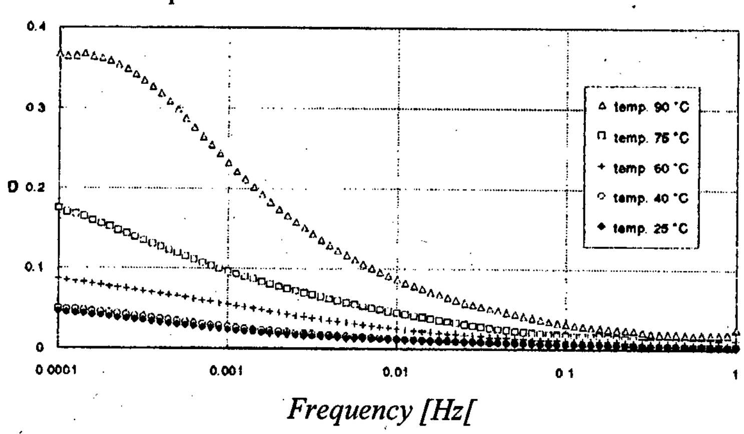
For the industrial diagnostic methods, it is important to find a physical parameter p for an insulating material which could be affected by time and/or temperature. Measuring the property p as a function of time or temperature - the so called aging effect - one might evaluate a degree of degradation with exposure time and temperature. It has been observed that the physical and chemical changes caused by time and/or temperature influence the complex permittivity.

This paper presents transient current investigation on power cable junction and rubber strip. We have carried out systematic measurements of dielectric constant and dielectric absorption on power cable junction and rubber strip in the frequency range 10'4 Hz to 1 Hz. Evidence of decreasing dissipation factor with time for short aging time and increasing after long aging time is presented. Our results show that the measurement of the dissipation factor and the relaxation frequency in the low frequency region is an useful way to estimate the degradation of the power cable junctions and rubber strips.



Frequency dependence of the junction loss factor D for different temperatures.

We intend to discuss theoretical models linking dielectric parameters with physico-chemical and thermal degradation of the power cable junctions and rubber strips. Thermally activated chemical and/or structural changes on the polymer and rubber molecules are caused by chemical reactions. These processes induce irreversible material deterioration which can be measured using different0.0001 0.001 0.01 0.1 1diagnostic methods. Therefore, it seems natural to approach a problem of thermal aging theory using chemical kinetic equation which involves time factor and very known Arrhenius model which involves temperature one. Cornbining both approaches one can get relation which could be a measttre of the degree of degradation of material. We have proposed particular choice of a property p far both the power cable junction and rubber strip and theoretical background which may be useful to understand physical-chemical thermal degradation.

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SIMULATION OF DIELECTRIC RELAXATION EFFECTS IN BULK POLYMERS

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Both relaxation times and relaxation amplitudes of the dielectrically detected relaxations in polymers depend on details of localization and orientation of dipole moments within molecular units (usually monomers) as well as on possible dipole-dipole correlations resulting from structural correlations between these elements. Such effects are usually not precisely considered in interpretation of the dielectric spectroscopy results, however, they can cause large deviations of the observed relaxation rates and amplitudes from these detected by other relaxation spectroscopies (e.g. mechanical, optical or NMR). In this paper, possible differences between observations of relaxation processes performed by various experimental methods will be discussed on the bases of an analysis of computer simulated melts of polymers consisting of segments with various localization of dipole moments. Effects resulting from macroscopic and microscopic orientation correlations like, for example, in microphase separated block copolymer systems will be considered. Dynamic simulations of macromolecular dense systems are performed using the cooperative motion algorithm (CMA) which allows monitoring of dynamic correlations of various structural units. From the recorded dynamic correlation functions, relevant to quantities observable by various experimental methods, relaxation times are determined. Simulation results will be compared with experiments, for some cases.

HIGH-FREQUENCY DIELECTRIC DEPENDECIES OF POLYMER MATERIALS

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The dielectric relaxation of polymer systems in high-frequency region 10 kHz-1GHz has been investigated. It is found from dependence of relaxation time on the concentrations of crosslinks that the relaxation mechanism is ascribable to the diffusion process around the charged backbone network. The dielectric relaxation spectroscopy has revealed the details of Coulombic field in polymer which is saturated to an almost constant value.

NUMERICAL METHODS IN CALCULATIONS OF ELECTRODINAMICAL PROPERTIES OF METALLIC COMPOSITES.

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The physical properties of metallic composites have been the subject of much recent interest. In particular the effect of shape and environment has been studied through their response to an electromagnetic excitation. The first influences the polarizability and the second the local field each particle of composite is in. In particular we treat the case of a particles of composites in the presence of one or more excitation whose wavelength is much larger than the particle diameter and interparticle separation. Shape and bulk properties are introduced through the particles polarizabilities.

A satisfactory solution to this problem is not necessarily simple since it must be self-consistent in the sense that the effect of environment on a given particle changes the response of the environment itself. Also there is the question of convergence in the multipole coupling between particle and environment that occur. The validity of the usual dipole approximation has been questioned by several authors when the particles are very close. We have provided calculations including higher multipole interactions between particles of metallic composites, and develop here a theory that yields a straightforward computational scheme for obtaining the normal modes of the system to an arbitrary pole order assuming only that polarizabilities are known. While studing of resonances spectrum it is noted that with volume fraction increasing the pair multipole interactions between particles become significant. We have also developed a straightforward scheme of effective dielectric constant calculation of metallic composites with application of exact Percus-Yevick distribution function.

SPLITTING BETWEEN MAIN AND SECONDARY RELAXATIONS IN MONO-, DI-, AND TRI-EPOXY COMPOUNDS

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Wideband dielectric spectroscopy (10^2- $2\cdot10^{10}$ Hz) was used to study the dynamics of mono-, di-, and tri-epoxide compounds from below to above the glass transition temperature, T_g . Dielectric spectra above T_g revealed the existence of two relaxations, a structural and a secondary process, which merge at the splitting temperature T_s, located some tenths of degrees above T_g. A d.c. conductivity contribution is also present. The glass transition phenomenon markedly affects the temperature dependence of both the dielectric strength and the low frequency slope of the secondary process. The prediction of the Stokes-Einstein-Debye (SED) model was verified for mono- and di-epoxide, while a fractional power law (FSED) replaces the SED relation in tri-epoxide for T<Ts. Moreover, a transition temperature $T_B \cong T_s$ between two different Vogel-Fulcher regimes was recognised in all systems. The overall picture of the dynamics of the systems is enriched and very recent ideas on the splitting between main and secondary relaxations are confirmed. Finally, the triepoxy compound shows an additional relaxation, which is masked by the conductivity contribution and it is slower than the structural one. Such relaxation seems to be related to the conductivity and it is found to follow the FSED law.

ANTIREFLECTION AND PASSIVATING COATINGS ON THE BASIS OF RARE EARTH ELEMENT OXIDES FOR SILICON DEVICES

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Among the materials that are prospective for the usage as antireflection coatings of silicon photoelectric devices (REEO) rare earth element oxides have a big advantage as they have high transparency in the working range of spectrum, high thermal and chemical stability, and their refraction index is optimum for this purpose. The investigations conducted have shown, that the deposition of a REEO film on the surface of silicon allows to reduce the spectral index of light reflection from the silicon surface down to 0.01-1.2 % and to increase the spectral value of short-circuit photocurrent of a silicon photoelectric transducer more than by 50%. An important requirement for optical coatings of semiconductor devices is the ability to obtain the interface with a semiconductor, that has low recombination losses. That is why in this paper the effective life time and the surface recombination rate of nonequilibrum charge carriers in silicon wafers, passivated by the films of some REEO were investigated.

The cerium, dysprosium, yttrium, gadolinium and ytterbium oxide films were fabricated on both surfaces of a single-cristalline silicon wafer doped by fluorine, with the resistance of 20 SZ cm and (100) orientation by thermal oxidation of the predeposited rare earth metal layer, in the air at 400 °C for 30 minutes. For the determination of effective life-time i and the surface recombination rate S the photoconductivity relaxation after the irradiation of the sample by rectangular light signals technique was used. The temperature dependences of the effective life-time were measured in the temperature range of 290 - 410 K . In order to exclude the influence of nonequilibrum charge carriers trapping effect on the surface and in the bulk of the semiconductor the effective life-time measuring was conducted at a temperature of ~400 K . Table presents the obtained values for the surface recombination rate for silicon samples before and after the deposition of a REEO film.

Table

Effective life - time and surface recombination rate values in silicon at a temperature of 400 K

Film medium	W-out film	CeO_2	Dy_2O_3	Gd_2O_3	Yb_2O_3	Y_2O_3
τ, μs	18,5	24	50	54	58	54
S, sm/s	920	720	340	330	290	310

The results presented prove that the surface recombination rate decreases after the deposition of a REEO film. Besides the comparison of the recombination characteristics obtained show that the surface recombination rate in the Si -REEO system is of 1-2 orders of degree lower than the analogous parameter in the Si - SiO_2 and Si - $SiOI_2$- Si_3N_4 devices that are widely used in semiconductor electronics.

ELECTROPHYSICAL PROPERTIES OF THE SWITCHING MIS-STRUCTURES WITH REE FLUORIDES

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The results of the investigation of the electrical switching with memory effect in MIS-structures with rare earth element (REE) fluoride films are presented.

The REE fluoride powder was thermally deposited (in vacuum) onto a single-crystal silicon substrate with the charge carriers' concentration $n = 9\cdot10^{14}$ cm^{-3} and $p = 3\cdot10^{15}$ cm^{-3} for the substrates with electron- and hole- conductivity types respectively. It was revealed that the electrical conductivity switching effect in the structures with REE fluorides is characterized by the high factor of resistance magnification between high- and low-resistance states ($10^6 - 10^7$), the short time (fractions of μs) and energy ($\sim 10^{-8}$ Joule) of switching.

The mechanism of the memory conductivity switching is suggested. The transient characteristics of switching, the dependence of electrical parameters of switching on the temperature regimes, dielectric shape and dimensions, voltage polarity, etc. were the subject of investigation, that made it possible to identify the electrothermal nature of the switching effect in these structures.

The change - over of the structure from a low-ohmic state into a high-ohmic can also be carried out by the thermal method both during application of voltage and by heating the samples without applying voltage at a temperature of $\approx$ 400-430 K. The investigated structures can be used as electric and thermal switches as well as fixed reprogrammable memory devices. The specialties of volt-amps, volt-farad and photoelectric characteristics of MIS-structures in the high- and low-resistance states were determined. It is determined that the volt-amps characteristics of MIS-structures in the dielectric state are described by the Poole-Frenckel mechanism, and their volt-farad characteristics are identical to the typical high-frequency volt-farad characteristics of MIS-structures.

After the switching to a low-resistance state the volt-amps characteristics start to have an unipolar shape with the rectification index of $10 \div 10^4$, and the volt-farad characteristics in the low-resistance state represent the non-equilibrium depletion region at a reverse bias. The difference in the capacitance values of the structure in the accumulation region in the high- and low-resistance states does not exceed 15 pF, indicates that the changes in the structure during the switching process take place locally.

The study of photoelectric characteristics of MIS-structures in the low-resistance state proved the possibility of the injection amplification of photocurrent in them. It is shown that in the low-resistance state the electrophysical characteristics MIS-structures are analogous to the characteristics of the metal-tunnel electricsemiconductor structures.

Silicon MIS-Structures with Rare Earth Oxide Films as Insulator

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The electrical and photoelectrical properties of silicon MIS-structures with Rare Earth Element (REE) oxides as dielectric were investigated.

The samples were fabricated on silicon monocrystalline wafers of n and p conductivity types. The dielectric films were obtained by thermal oxidation of the rare earth metal layer in the air at a temperature of 500-550 °C. The rare earth metal was deposited onto a silicon substrate by thermal evaporation technique from a molybdenum vessel at 10^{-3} Pa vacuum level. A semitransparent aluminium or nickel electrode covering the square of 0.39 10^{-3} cm^2 was deposited onto the REO film by thermal evaporation in vacuum through a mask.

The capacity of the samples at a frequency of 1 MHz decreased approximately from 160 to 40 pF with the variation of direct voltage from -3V to +3V. The hysteresis of the volt-farad characteristics on the voltage axis was 0.2-0.5 V. The surface states' density and the fixed charge in the dielectric were equal to (2.4-4) 10^{11} cm^{-2} eV^{-1} and (4-7) 10^{-8} C'cm^{-2} respectively.

The energy barriers on the interfaces were equal to: Al-Yb_2O_3 (2,90-2,92 eV), Ni-Yb_2O_3 (3,30-3,32 eV), Si- Yb_2O_3 (3,18-3,20 eV). They were evaluated out of spectral characteristics of photocurrent by the threshold of internal electron emission.

When Al- Yb_2O_3-Si structures were irradiated by UV-light with the photon energy higher than 5.2 eV, the volt-farad characteristics moved along the voltage axis towards positive values at both bias polarities. This result proves that the trapping of electrons on deep traps in Yb_2O_3 took place. The dependences of on the irradiation time are of sub-linear type with a tendency of saturation at large irradiation time (~ 1 hour). The rate of the flat-band voltage shift change increases together with the increase of the bias applied to the structure. The trapped charge was preserved for a long time at a room temperature after light and direct voltage were switched of The value of the charge trapped in the dielectric is by one order of degree lower than the charge that has passed through the structure. During the irradiation of the structures by light the photocurrent decreases with time reaching a stationery value. The observed kinetics of photocurrent is explained by photoinjection and the trapping of

electrons to dielectric. The charge carriers trapped in the dielectric decrease the electrical field in it. This leads to the decrease of photocurrent through the structure.
By using the method of photostimulated depolarisation the energy depth of electron traps in the dielectric film was determined. It was found that the electron trapping centres are situated 2.4-2.7 eV below the conductivity band bottom of Y_2O_3. The 'centroid' of the trapped charge during the irradiation of the structures is situated almost in the centre of the dielectric layer.
The prospectivity of the usage of the studied structures as varicaps is shown.

ELECTRIC FIELD DEPENDENCE OF TRANSIENT CURRENTS PROFILES IN SPATIALLY NON-UNIFORM DIELECTRIC LAYERS

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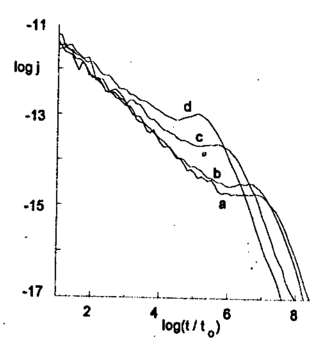
Recently, in a series of papers the Monte Carlo calculations of the time-of-flight transient currents for *r*- and *r*-ε-hopping transport in spatially non-uniform layers have been presented [1-4]. The total density of localised centres was assumed to depend exponentially on the distance from the layer contacts. A remarkable influence of the spatial non-uniformity of the hopping centre distribution has been described and discussed in detail. Since in the previous work we concentrated ourselves on the influence of spatial non-uniformity on the current profiles, carrier jump statistics, and the carrier packet evolution in space and time, the calculations in [1-4] were performed for only one value of the external electric field E. In the present contribution we report on the Monte Carlo simulation of the time-of-flight transient currents in spatially non-uniform layers in a wide range of electric fields. The field dependencies of the effective time-of-flight, dispersion degree, jump statistics are discussed in detail. It turns out that the characteristic current maxima occurring in layers with the hopping centre density increasing between injecting and collecting electrode just before the effective time-of-flight disappear in the low field limit. The relative height of the current peaks initially increases on increasing field, and tends to a saturated value for higher fields. As an illustration, several current transients calculated in a spatially non-uniform layer for various values of the external field intensity are shown in the figure below.



R-ε-hopping transient currents in a layer with the centre density increasing exponentially (e^2 times) between injecting and collecting contacts for several values of external field: a: $E = 5\cdot10^6$ V/m, b: $E = 10^7$ V/m, c: $E = 5\cdot10^7$ V/m, d: $E = 10^8$ V/m.

The opportunity to perform our MC simulations at the TASK Computer Centre in Gdańsk is kindly acknowledged.

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THE INFLUENCE OF OFF–DIAGONAL DISORDER ON STATIONARY CURRENT–FIELD CHARACTERISTICS IN HOPPING SYSTEMS

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Phonon-assisted hopping of electrons between spatially distinct locations is one of the basic transport mechanisms in solids [1-3]. The hopping mechanism dominates in low-mobility systems, such as weakly doped or strongly compensated semiconductors, amorphous solids, glasses, organic solids, or transition metal oxides. In the present contribution we discuss the current - field, and differential conductivity - field characteristics in model systems with no on-diagonal disorder in their dependence the on degree of pure off-diagonal disorder. We limit ourselves to the electron transport close to the Fermi level. The numerical calculations of current-field characteristics were performed similarly as described in [4-5].

In order to investigate the influence of the off-diagonal disorder on the current-field characteristics, the numerical calculations have been performed for the sequence of the centre distributions obtained as distorted simple-cubic lattices. In particular, the nodal positions were shifted at random within a cube of the edge equal to $p \cdot a$, where a is the cubic lattice constant, and p = 0.1, 0.2,..., 0.9, 1.0. Figure 1 shows the current-field characteristics calculated for systems of various degrees of the off-diagonal disorder, and for various dilutions α, where α is defined as the ratio of the average distance between centres to the centre localisation radius. Figure 2 shows the corresponding field dependencies of the differential conductivity. In both Figures the normalised field E' is defined as $E' = qE/2\alpha kT$. As it is seen, although the influence of increasing off-diagonal disorder (increase of p) is qualitatively similar for each dilution, there are significant quantitative differences. In strongly diluted systems the current values increase by several orders of magnitude for p increasing from 0 to 1. Such a behaviour is related to the fact, that in more distorted systems the carriers find more easily an extremely effective percolation cluster which dominates all other paths. In dense systems the dispersion between the conductivities of different current paths is lower, and the changes of the current values in the function of p in much smaller. The plots of the differential conductivity (Figure 2) reveal the appearance of the conductivity minima for sufficiently disordered systems. At given dilution α the minimum appears at higher fields in more disordered samples (greater p), whereas at fixed value of the p parameter the field corresponding to the conductivity minimum is higher for less diluted centre distributions. The detailed analysis of the current paths shows that from fairly low p values on (from $p \approx 0.3$), there appears a single dominating path with few returns against the field that carries almost all the electric current.

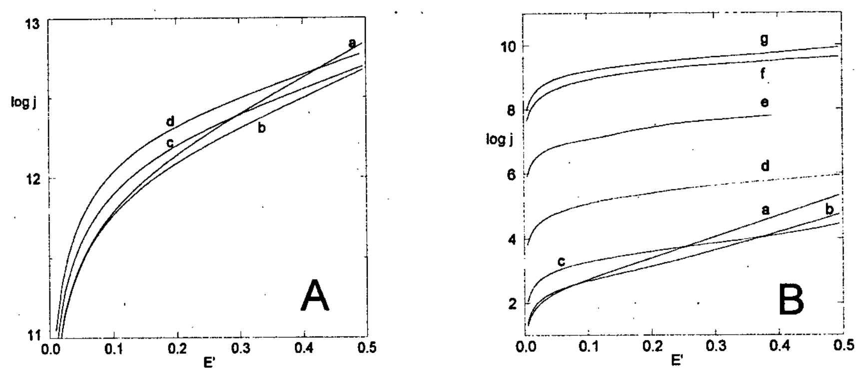

Figure 1. Current-field characteristics calculated for systems with no on-diagonal disorder for various degrees p of the off-diagonal disorder, and for various dilutions α. A: $\alpha = 5.0$; a: centres in nodal positions of a simple cubic lattice ($p = 0$); b: $p = 0.5$; c: $p = 1.0$; d: totally random centre distribution; B: $\alpha = 15.0$; a: $p = 0$; b: $p = 0.2$; c: $p = 0.4$; d: $p = 0.6$; e: $p = 0.8$; f: $p = 1.0$; g: totally random centre distribution.

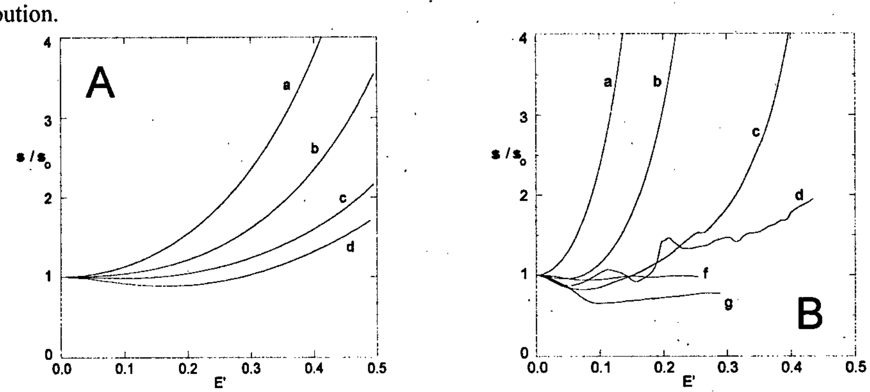

Figure 2. Field dependence of the differential conductivity calculated for the curves of Figure 1. A: $\alpha = 5.0$; B: $\alpha = 15.0$.

The opportunity to perform our MC simulations at the TASK Computer Centre in Gdańsk is kindly acknowledged.

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COMPUTER INVESTIGATION OF LOCAL ORDER AND LONG–RANGE CORRELATIONS IN DILUTED RANDOM GRANULAR SYSTEMS

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Random packings of hard spheres in three dimensions have been studied extensively throughout several past decades. Random close packed sphere distributions were used to represent the structure of liquids and glasses, to provide structural models to investigate phenomena such as fluid flow, stress distribution, particle-size segregation, or electric conductivity of metallic powders. Much effort has been dedicated to establish the maximum packing of identical spheres, and to elucidate the nature of the geometrical frustration in random systems. However, geometrical properties of systems of disjoint spheres, which have random radii, and which occupy a rather small total volume fraction, have been investigated to much less extent. Since such a sphere distribution corresponds closely to the distribution of metallic granules in some hydrogen reduced oxide glasses, a detailed study of the geometrical properties of the random sphere systems should be relevant to the interpretation of conductivity measurements in these materials.

In the present contribution we describe two algorithms for generating of random three dimensional diluted systems of disjoint spheres. In the first algorithm produces the spheres of a given (*e.g.* taken from the experiment) distribution of radii and a given occupation fraction. In the second algorithm the density of nucleation centres, the nucleation mechanism, and the occupation fraction are assumed, so that the radii distribution in the resulting configuration can be calculated only after the construction procedure is completed, and then compared with experimental results. The model sphere distributions obtained within both methods are analysed in terms of pair-correlation functions, structural factors, co-ordination numbers, and Voronoi polyhedra statistics. The stochastic properties of clusters of granules are also described. The results of our model calculations are used to explain the dependence of the conductivity - temperature characteristics on reduction conditions in bismuth glasses.

'he opportunity to perform our MC simulations at the TASK Computer Centre in 'ańsk is kindly acknowledged.

STUDY OF POLARISATION AND CONDUCTIVITY MECHANISM IN PHOTOCHROMIC GLASSES

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Photochromic glasses are known from many years. Silver halide glasses are used as spectacle glasses. Another type of photochromic glasses are glasses with copper and cadmium halides. These glasses can be applied as an information carrier of multiple use. They have relatively short darkening period and a very prolonged bleaching period. To obtain precipitates of halide microphase which is a photochromic carrier, glasses are additionally submitted to heat treatment.

In this paper we apply thermally stimulated currents (thermally stimulated polarisation TSPC and thermally stimulated depolarisation TSDC) method to investigate of structure of copper halide glasses. The thermally stimulated currents were measured in the range 100-450K.

The subject of investigation was sodium borosilicate glass containing halides of copper and cadmium. The glass underwent the heat treatment at 600^0C for different time (0.25, 1 and 2 h).

The dc conductivity values were calculated from TSPC-2 curve. Starting from low temperature and polarising glass at successively higher temperatures 3 TSDC peaks are observed. The magnitudes of peaks are different in glass submitted to different heat treatment.

The changes observed in dc conductivity and TSDC peaks as a result of heat treatment are attributed to the structure of investigated glasses. The low temperature peak can be related with orientation sodium ions around $[AlO_4]^-$ or/and $[BO_4]^-$ groups. It can be supposed that peak P2 is attributed to translation motion of sodium ions in sodium-boron rich phase. The appearance of P3 peak can be connected with existence of the particles of photosensitive phase.

The electron micrographs, investigations of added optical density of glass with photochromic compounds and TSPC/TSDC measurements of glass without copper and cadmium halides confirm this interpretation.

CRITICAL DYNAMICS IN THE ISOTROPIC PHASE OF NEMATOGENS AND SOLUTION OF LIMITED MISCINILITY TESTED BY NONLINEAR DIELECTRIC EFFECT MEASUREMENTS.

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A liquid system on approaching its critical point may becomes literally soft due to the strong divergence of the susceptibility (χ) of the order parameter (M). The dynamics of such systems is associated with large - length, long - lived critical fluctuations. In this report we present results of studies of critical dynamics in binary solution of limited miscibility (nitrobenzene - dodecane) and in the isotropic phase of nematogens with the different position of the permanent dipole moment (8CB and MBBA) using the nonliner dielectric effect (*NDE*). The possibilities of this research method for such studies are associated with the fact that $NDE \propto \left\langle \Delta M^2 \right\rangle_v \times \chi$ both in critical solutions and in the isotropic phase of nematogens [A. Drozd-Rzoska et al., *Phys.Rev.* E54 (1996) 6452]. However, in critical solutions fluctuations are strongly interacting, whereas prenematic one seems to be exhibiting gaussian characteristic. In both cases the same dependence of the relaxation time $\tau \propto (T - T_C)^{-1}$ [S.J Rzoska et al., *Phys.Rev.* E56 (1996) 2578 and Drozd-Rzoska, *Liq.Cryst.* (1998) in press.) has been approximately found . It may indicate on the same value of the dynamic critical exponent z for both types of systems. For a given distance from a critical point the stretched-exponent describing the time decay of fluctuations is equal to $x = 2/5 - \eta \approx 0.39$ (η is the exponent for the correlation function) in critical solutions and $x = 1$ in the isotropic phase of nematogens. It is noteworthy that such behaviour is strictly system independent, universal. The obtained data made also possible to test the Onuki - Doi model [*Europhys.Lett.* 17 (1992) 63] and the generalized droplet model [R. Piazza et al. *Phys.Rev.* B38 (1988) 7223] predictions. Studies were conducted under atmospheric pressure, as a function of temperature and isothermally, as a function of pressure (up to 250 MPa). This allowed to test the possibility of the isomorphic behaviour of the

complex relaxation of critical fluctuations for mentioned paths of approaching the critical consolute point. Additionally the obtained results strongly support the recently proposed by Mukherjee et al. [*Phys.Rev.* E51 (1995) 5745] idea of the fluidlike, critical behaviour in the isotropic phase of nematogens.

The applied, newly reconstructed NDE apparatus [M. Górny et al., *Rev.Sci.Instrum.* 67 (1996) 4290] made it possible to conduct tests in three modes: in the time - domain after switching-off the strong steady electric field and in the frequency - domain as a function of a weak measuring field (60 kHz - 12 MHz) and as a function of the frequency of the strong, electric field (DC - 2 kHz).

Studies conducted under project 2 PO3B 030 12 (KBN, Poland).

TEMPERATURE AND PRESSURE STUDIES OF "LINEAR" AND "NON-LINEAR" DIELECTRIC RELAXATION IN AN EPOXY RESIN

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In the strong electric field dielectric permittivity ceases to be field-independent: $\varepsilon^E = \varepsilon + \varepsilon_1 E^2 + \ldots$. The measure of the nonlinearity is the nonlinear dielectric effect: $NDE = \left(\varepsilon^E - \varepsilon\right)/E^2$. In this report we present results of ε and time-domain NDE studies in supercooled and superpressed state of an epoxy resin (diglycidyl ether of bisphenol A) up to 350 MPa. Basing on the analysis of the τ(P) behaviour determined form „linear" (ε) measurement the influence of the pressure on the value of the glass transition temperature has been found. The temperature, isobaric data can be portrayed by the Vogel - Fulcher - Tammann (VFT) law whereas the two-parameter equation $\tau = \tau_0 \exp\left(CP/\left(P_0 - P\right)\right)$, where P_0 is the ideal glass transition pressure and τ_0 is the value of the relaxation at atmospheric pressure, portrays the pressure, atmospheric data.

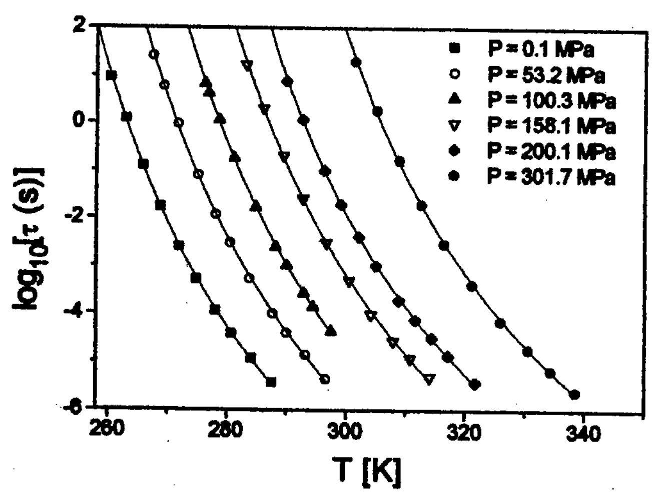

Fig.1 Temperature dependence of „linear" dielectric relaxation times for different pressures in the tested epoxy resin. Solid lines present the VFT fit.

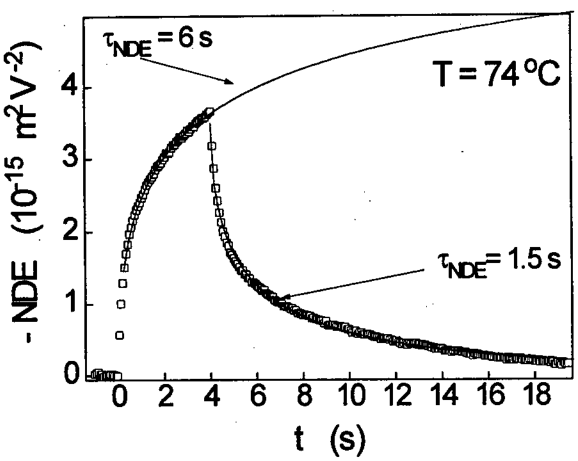

Fig. 2 An exmpale of the responce of the tested epoxy resin sample on the action of the AC rectangular pulse of strong electric field (E = 10^4 Vcm^{-1}, duration Δt = 4 s). The parameters of the weak measuring field E_m = 3 Vcm $^{-1}$ and f_m = 1.2 MHz. Solid lines represent KWW fit. Relaxation times are shown.

In *NDE* studies the shift in the dielectric permittivity due to the application of a rectangular pulse (duration 0.5 - 256 s) of a strong electric field was detected. The deformation of the pulse associated with relaxation processes in the resin can be well described by the stretched - exponential function. The obtained here relaxation times (τ_{NDE}) are definitively much longer than ones obtained from „linear" measurements. Additionally, they seems to diverge in the vicinity of T_g whereas relaxation time from „linear" spectroscopy" diverge at ideal glass temperature T_0.

Studies were conducted under 2 PO3B 030 12 project (KBN, Poland).

COMPATIBILITY STUDIES ON SOME POLYMER BLEND SYSTEMS BY ELECTRICAL AND MECHANICAL TECHNIQUES

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Systematic electrical and mechanical studies were carried out on natural rubber (NR) blended with different types of synthetic rubber such as styrene-butadiene rubber (SBR), polybutadiene rubber (BR) and ethylene propylene diene monomer (EPDM) as non-polar rubber; nitrile rubber (NBR) and chloroprene rubber (CR) as polar ones. The NR/SBR, NRBR, NR/EPDM, NR/NBR and NR/CR blends were prepared with different ratios namely 100/0, 75/25, 50/50, 25/75 and 0/100. The permittivity (ε') and dielectric loss (ε") of these blends were measured over a wide range of frequency (100 Hz-100 kHz) and at room temperature (≅ 27°C). The results of compatibility obtained from the dielectric measurements are comparable with those obtained from the calculation of the heat of mixing. These results show that NR/SBR and NRBR blends are compatible while NR/EPDM, NR/NBR and NR/CR blends are incompatible. To overcome the problem of phase separation (incompatibility) between NR and EPDM, NBR or CR, a third component such as SBR or poly (vinyl chloride) (PVC) was added as a compatibilizing agent to these blends. The experimental data of dielecric and mechanical measurements show that the addition of either SBR or PVC could improve to a great extent the compatibility of such blends.

THE INFLUENCE OF CENTRAL BRIDGE GROUPS ON THE MECHANISM OF DIELECTRTG POLARIZATION OF LIQUID CRYSTALS

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The intluence of central bridge groups of molemle on dipole structure and molecular mechanisms of dielectcic pola.rization of nematic liquid crystals (LC) in the frequency range of $10^2 - 10^8$ Hz was experimen-tally investigated.

It was established that substitution of high polar bridge groups instead of weakly polar bridge groups lead to increasing of dipole moment of molecule and anisotropy of dielectric permittivity. The low frequency dependence of permittivity anisotropy $<\varepsilon = \varepsilon_{11}-\varepsilon_{1}$ is related to the dispersion of the dielectric perrnittivity ε_{11} parallel to the director for liquid crystal. Here ε_{1} is the dielectric permittivity perpendicular to the director. The strong dispersion of ε_{11} is connected with a exclusion of the contribution from the orientational dipole polarization of LC of the rotation of the polar molecules around their short transverse axes. The relaxation processes LC materials are quantitatively described by the Debye dispersion curves with single dipole relaxation time. It was shown that such substitution lead to decreasing of frequency dispersion of dielectric permittivity in nematic and isotropic phases.

The components of dipole moment, relaxation times and activation energies of rotation movement around their short and long axes were calculated.

It was established that substitution of high polar bridge groups instead of weakly polar bridge groups lead to changing of the angle between dipole moment and longitudinal axis of molecule. Investigations of liquid crystals with different central bridge groups allow to obtain a very important information concerning the relation between chemical structure of molecule and mechanisms of dipole polarization.

THE INFLUENCE OF X- RAY IRRADIATION ON DIELECTRIC PROPERTIES OF THERMOTROPIC LIQUID CRYSTALS

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In the present work an influence of X-ray irradiation on thc dielectric properties of different type termotropic liquid crystals {LC) mesomorphic and isotropic state haue been investigated. It was established that X-ray irradiation doses which were used in our experiment did not change the phase transition temperatures of LG samples. Moreover, all the amendments of the conductivity values of the samples under the X-ray irradiation effect were completely reversible after the switching off the radiation source. So on the base of experimental results, we can climed thet the power doses up to 1,2 Gy/s do not cause a significant destruction of LC samples (in contrast to gamma and proton irradiation [1,2]) and, therefore, radiation induced impurities are nat an origin of the changes which praduced an eiiect of additional conductivity of Lcs.

It was shown that the value and sign of additional electric conductivity<1 $\sigma=\sigma-\sigma_0$ (here σ and σ_0 a conductivities of the sample affected by X-ray irradiation and without it respectively) of LC samples arising under X-ray irradiation depend on the value of their intrinsic conductivity σ_0. Indeed, for all the LCs with the high σ_0 value the additional conductivity values <1 σ are negative in sign under varying the X-ray irradiation pawer doses. On the contrary, if the σ_0 value decreases along with the temperature fall or intensification of the sample clearing degree one can observe an invertion of < 1 σ sign from negative to positive when the samples σ_0 value is sufficiently low.

The possible reasons of the observed beheviour of additional electric conductivity in LCs under X-ray irradiation are discussed.

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DIELECTRIC DILATOMETRY ON THIN TEFLON-PTFE FILMS PREPARED BY PULSED-LASER DEPOSITION

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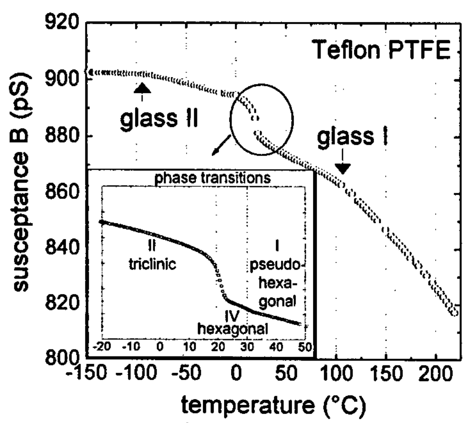
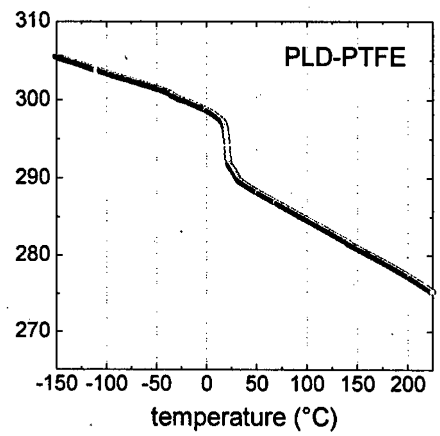
Nonpolar polymers, such as Teflon PTFE are attractive for high-performance microelectronics and electret device applications, due to the low dielectric constant, small dielectric losses, and excellent charge storage capability. These applications require thin polymer films on various substrate materials. However, the remarkable processing difficulties of Teflon make the preparation of thin films a challenging task. One reason for the often reported poor quality of PTFE-like films seems to be the more or less gradual deviation of the chemical structure of the resulting films from Teflon PTFE. These deviations are for example due to chemical contamination, extensive lowering of the molecular weight, oxidation, and fluorine deficiency.

In this contribution, pulsed-laser-deposition (PLD) [1], which is a rather novel technique in the field of polymer film fabrication, has been employed for the preparation of thin Teflon PTFE-like films [2]. Thin films from two different targets are reported and compared with respect to PTFE-specific properties in the films, e.g. structural phase- and glass-transitions.

It will be shown that PLD of PTFE from suitable chosen targets permits to produce highly crystalline thin films with characteristics remarkably similar to those of bulk PTFE: Thus, PLD opens new possibilities for applying thin polymer films in microelectronic and electret devices.

For a comparison of polymer films obtained by different techniques, the identification of specific structural phase- and glass-transitions is highly demanded. Such volumetric transitions are most often investigated by methods like mechanical dilatometry and scanning differential calorimetry. However, these techniques are difficult to apply for thin films on substrates. For example, in a 1 μm thick film, the change in film thickness is only of the order of 1Ĺ/°C. Such small thickness changes are extremely difficult to resolve. It will be shown that in thin nonpolar polymers, dielectric dilatometry, e.g. the measurement of the susceptance as a function of temperature is a versatile tool for resolving such small changes in the film thickness.





Therefore, dielectric dilatometry can be applied for the determination of structural phase- and glass-transitions in polymers and also for the measurement of the linear thermal-expansion coefficient in constrained thin-film geometries.

Teflon PTFE is known to show at least four volumetric transitions, two first-order structural phase transitions and two glass-transitions. This is shown in Fig. 1(left), where the susceptance B of a 25μm thick PTFE foil is depicted within the temperature range from -150°C to 250°C. The glass II and I transitions are observed around -90°C and 110°C, respectively. The structural phase transition from a triclinic to a hexagonal lattice is found at 19°C, and to a disordered pseudohexagonal lattice at 32°C, as known from the literature [3]. The excellent agreement with literature data demonstrates the versatility of dielectric dilatometry for the investigation of volumetric transitions in nonpolar polymers.

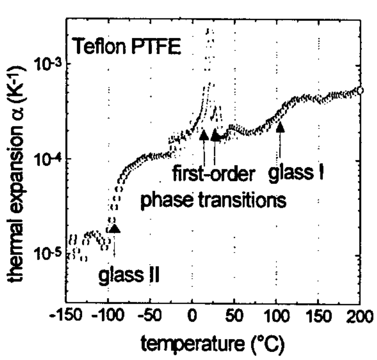


Fig. 1(right) shows the susceptance B of a 14μm thick PLD Teflon film from a press-sintered target. Only the two structural phase transitions are clearly resolved. The glass-transitions which are associated to the amorphous regions are absent in the high-crystalline sample. The high crystallinity of the PLD films has also been confirmed in infrared transmission spectroscopy.

Additionally, the linear thermal expansion coefficient can be determined for the two Teflon films, as shown in Fig. 2(left) and (right). The thermal expansion follows from the susceptance by taking into account the temperature dependence of the dielectric function via the Clausius-Mossotti equation.

To summarize, PLD Teflon films with excellent quality and high crystallinity have been prepared. Dielectric dilatometry has been proved useful for the thermophysical characterization of nonpolar polymer films. The PLD-PTFE films seem to be most promising for electret applications, as first experiments also show excellent thermal stability of charged films.

Financial support by the Fond zur Förderung der wissenschaftlichen Forschung (FWF) in Austria is gratefully acknowledged.

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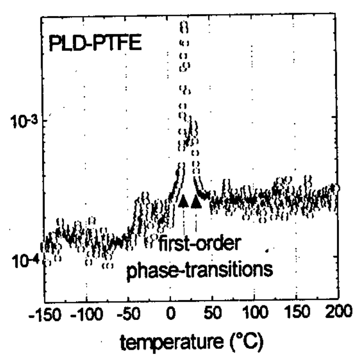

THE THERMO- AND X-RAY LUMINESCENCE OF $LaMgB_5O_{10}$ GLASSES DOPED BY (Ce, Gd, Pr, Eu).

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In last years more and more research has been concentrated on borate system. To date, the problem of synthesis of new scintillation materials with high output is important. The scintillation-luminescence properties $LaMgB_5O_{10}$ glasses doped by (Ce, Gd, Pr, Eu) are presented in paper.

The doping additives were chose with registration of attributes of famous effective scintillation materials. The doping additives were introduced into initial blend synthesized by solid-phase method. The concentrations of additives are changed from 0.5 to 1 at. %.

The X-ray luminescence and thermoluminescence spectra of irradiated and nonradiated samples are investigated. Possible types of energy transfer mechanisms are discussed.

RELAXATION PROCESSES IN DEFORMED LIQUID CRYSTAL LAYERS

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Relaxation of liquid crystal helix deformed by AC electric field (1kHz) was investigated. The investigations were carried out in the classical sandwich cell: ITO-cholesteric layer-ITO. Initial orientation of a helix axis was perpendicular to the surface with tilt angle of molecules equel 0°. It is shown that the relaxation processes include three modes: rapid, slow and intermediate ones. It was found that this intermediate mode may be approximized with exponential function:

$$C = C_0 \exp(-t/\tau)$$

in the case if appied voltage(V) was less than a cholesteric-nematic transition threshold(Vth) and the behavior of deformed helix is described by expression:

$$C = C_0 /((\beta+\gamma t)$$

in the case if V>Vth, where C - capacitance, τ,α,β,γ- constantes.

Two mechanisms of defective texture → initial state transition are discussed. It is shown that two channals(V<Vth and V>Vth) of transitions are in good agreement with following equations:

$$1)\ dC/dt = -C/\tau$$

$$2)\ dC/dt = \gamma C^2/\alpha$$

Because of the capacitance of the capacitor is defined by dielectric permittivity ε the equation 2 notes that this state of texture was more defective as well as the disclinations having different signs appeared.

DISCHARGE IN DISPERSIVE SYSTEMS UNDER OPEN-CIRCUIT CONDITIONS: COMPUTER SIMULATION

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The mobility measurements in low-mobility rnaterials with the time-of flight method under the closed circuit conditions started many years ago [1, 2]. The method has proved to be very fruitful research tool for the investigations of charge transport in low-mobility materials. However, sometimes the method cannot be used. For instance it cannot be used for thin films with inhomogeneities giving rise to short circuit when the top semi-transparent metal electrode is evaporated. In this case the discharge under open-circuit conditions may be useful. The measurements under open circuit conditions are carried out on a sample with one grounded electrode. The transport of charge takes place in the electric field produced by the charge injected at the free surface of the sample. The existing analytical solutions [3] refer to the charging of the free surface limited to a very thin layer at the very surface at the time t = 0. In this case the mobility is given by

$$\mu = L^2 /(V_0\tau) \qquad (1)$$

where L is the sample thickness, τ is the time at which $V = V_0/2$ and V_0 is the initial voltage. One of the assumptions leading to the above equation is that the charge transport is of Gaussian type and the trapping phenornena are negligible. If the initial volume of chargc is comparable with the sample volume and the transport is dispersive then the analytical solutions rather cannot be used. In order to solve the problem of charge transport in hopping systems under open circuit conditions for the dispersive type of charge transport and for the volume generation of charge a computer simulation of the problem has been carried out.

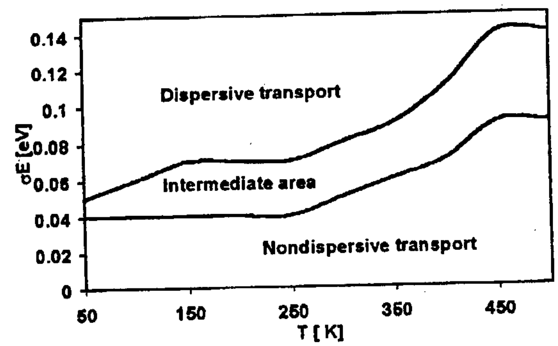

Fig. 1 The transition from non-dispersive to dispersive transport in the discussed hopping system.

The simulation has been carried out for the time-of flight method (i.e for the closed circuit) and for the open-circuit method. The method of simulation is a little similar to that presented by Bassler [3, 4]. The simulation system was a regular lattice of localized states containing 200 x 100 x 100 sites. The distance between states equals 3 nm which is suitable for typical low-conducting hopping systems. The assumed sample size was 0.6 μm x 0.3 μm x 0.3 μm. The density the localized states in the narrow band at the Fermi level is described by the normal distribution. The simulation has been carried out for the standard deviations of this distribution in the range 0.01 ÷ 0.2 eV, the assumed temperature range was from 50 to 500K. The simulation for the time-of light experiment shows that three types of charge transport may occur for the assumed values of parameters defming the sample(see Fig. 1). In the first area the transport is non-dispersive (Gaussian), in the second area the transport is dispersive, the third area is an intermediate area between the first two ones.

The simulation method of the open-circuit experiment is similar to the method used for the time-of flight experiment, though this is necessary to calculate the spatial distribution of the electric field for the open-circuit case. This simulation has been carried out for the depth of penetration equal 0, 0.2L, 0.4L, 0.6L, 0.8L, where L is the sample thickness.

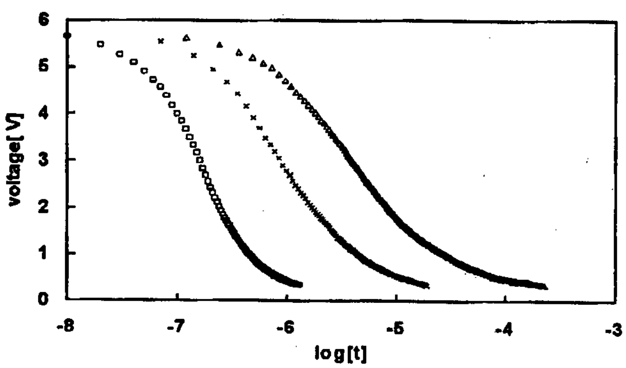

Fig. 2 Voltage versus time for various standard deviations of the energy distribution of localised states.□ σ_E=0.01 eV, x σ_E=0.07 eV, Δ σ_E=0.12 eV.

The initial spatial distribution of the generated charge was assumed to be uniform.. The results show that the discharging voltage depends on the depth of penetration of the generating electron beam. The value of mobility found from the discharging voltage curves for the volume initial generation of charge may be nearly twice as great as the real value of mobility. The obtained results enable to interpret the discharge under open circuit conditions in dispersive systems and for volume initial generation of charge.

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EPOXIDE CROSSLINKING STUDIES BY MEANS OF RECORDING OF ELECTRODE CURRENT

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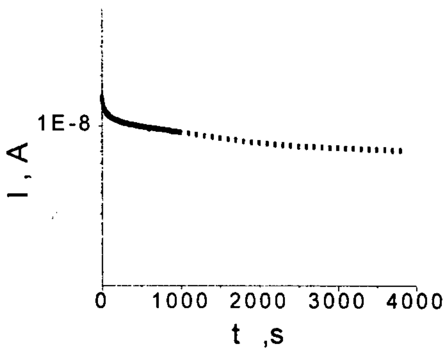
Monitoring of adhesive cure can be effected by means of recording of different physical values [1, 2]. Below, the results are reported about recording of sample electrical conductivity.

The idea of cure monitoring by means of recording of sample electrical conductivity is an old one. The method take an advantage of viscosity, η, and charge carrier mobility μ, relation, $\eta\mu$ = const, known as Waldens rule. This relation is often meet in viscous liquids.

In epoxide materials ionic species are assumed to be present as impurities. Therefore the number of carriers is assumed to be constant during cure reaction. The reaction of crosslinking of the material is alternating its viscosity. The viscosity change can be monitored by means of the measurement of sample conductivity. The above assumptions are valid if one carrier transport mechanism is operational. Therefore space charge polarisation, a phenomenon exhibiting strong time dependence, was a reason of using, instead of DC, AC conductivity recording. These measurements are used, exclusively, up to this moment.

However the use of electrode not exhibiting strong space charge polarisation phenomena, enables the use of DC technique to examine crosslinking reaction kinetics. The conductivity recording is carried in regime of electrode currents. These are believed to be the result of exchange the charge between electrode and material. The example of response of noncrosslinked sample of Epikote 828 is shown in Fig.1.

This is the case of the use of particular electrode material. In Fig.1 charging current I/ current flowing under DC voltage applied / vs time of measurement t is shown. As one can see from the plot the current is practically time independent. This is the proof that polarisation contribution to the current vs time dependence can be ignored.



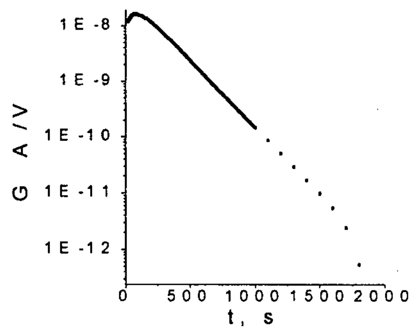


Fig. 1. Charging current I vs measurement time t recorded for noncrosslinked sample of Epikote 828. Sample thickness 0.2 mm, sample area 0.25 sq cm, voltage 1V, temperature 333K.

Fig.2. Sample conductivity G vs time of measurement t. Sample thickness 0.2 mm, sample area 0.25 sq cm, voltage applied 1V, crosslinking temperature 333K. Time of crosslinking T= t+900 s.

In present contribution sample conductivity G vs crosslinking reaction time t was recorded for several epoxide adhesives and mentioned above electrode. The materials under test were: Epikote 828 [3], Epidian-3, Epidian-5, Epidian-6 [4] with ethylene diamine [5] as crosslinking agent. Experiments were carried for stoichiometric as well as nonstoichiometric compositions. Particular result is shown in Fig.2.

In Fig.2 the result of crosslinking monitoring of Epikote 828 is shown. The plot of sample conductivity G vs time of measurement t in log-lin representation scales to straight line. This behaviour of G vs t dependence is similar to numerous records done by means of the use of AC technique.

The sources of possible errors are to be discussed. The results are compared with these related to cure monitoring by means AC technique.

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4. Ethylene diamine, commercial.

ON ELECTRICAL CONDUCTIVITY OF LIQUID CRYSTALLINE MATERIALS. OLD RESULTS IN LIGHT OF NEW FINDINGS.

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There exist a considerable literature related to electrical conductivity of liquidcrystalline materials. However, it seems that electrode interfacial phenomena were not taken into account in full. This would call severe criticism . This criticism is supported by frequency domain data. This data is indicating electrode polarisation as dominant mechanism, at elevated time, particularly.

For cyanobiphelyl materials electrical conduction process was analysed in details. Such parameters as sample conductivity and carrier mobility were determined as well as their anisotropy. From mutual measurements of sample viscosity and carrier mobility Waldens rule was checked and solvatation radious were evaluated. Unfortunately, in these investigations polarisation effects were not taken into account.

Now, it is clear, that at least in cyanobiphenyl materials, due electrode effects, DC conductivity is observed. However, in this case one can expect electrical field non-uniformity in the plane parallel /sandwich / sample. The aim of this contribution is the analysis of this effect and its relation on the results obtained in the past.

In the text, it would be analysed the data related to Frequency Domain as well as Time Domain investigation of the materials in test. The information content of both the methods as well as the source of possible errors will be discussed.

The aim of the communication is the critical evaluation of previously assumed material characterisation.

ON INTERFACIAL EFFECTS IN NEMATIC LIQUID CRYSTALS.

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Isothermal currents due to step voltage excitation were recorded in nematic as well as isotropic phase of liquid-crystalline material pentacyanobiphenyl /PCB/. Material in test was investigated as sandwich samples supplied by plane parallel electrodes. That was done by means of TD set up [1]. The transients up to 10 hrs were recorded. Additionally, sample discharging currents were measured. The use of Time-Domain dielectric spectroscopy technique was enabling to monitor evolution of polarisation /creating of space charge at electrodes/ process, from early stages till stationary conditions. It was enabling the evaluation of electrode current as a difference between charging and discharging current . It is shown that electrode current flowing at elevated time is almost time independent. The example is displayed at Fig. 1.

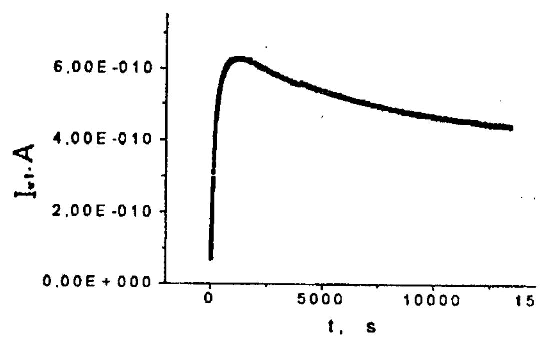
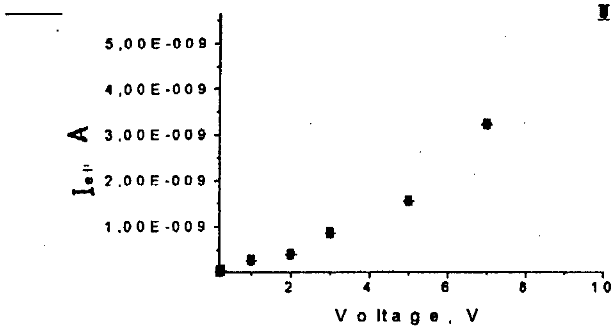


Fig.1. Electrode current in PCB sample, Au electrodes were applied , temperature of measurement 300.5K, voltage applied 1 V. Sample area 0.25 sq cm, sample thickness 0.2mm.

Electrode current is superlinear with voltage. Particular example is shown in Fig.2.

Fig.2. Electrode current vs voltage for PCB sample supplied with ITO electrodes. Temperature of measurement as and sample parameters as in Fig.1.



The data may be fitted to formula for Shottky emision currents. This mechanism is frequently observed in solid, weakly conducting organic solids. The results may be compared with that of Frequency Domain Data.

Charging plots recorded in PCB at 300.5 K by means of ITO electrodcs are shown in Fig.3.

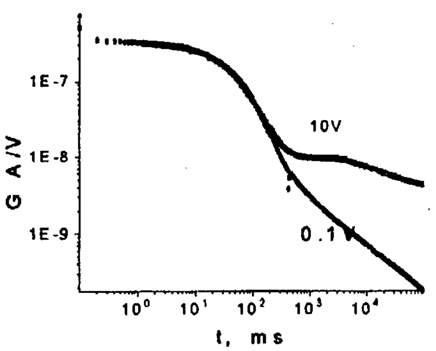


Fig.3. Conductivity recorded by means of TD set-up. Electrodes ITO, temperature 300.5K, 10 and 0.1 V applied to sample.

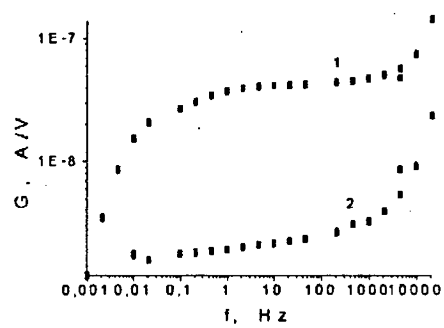


Fig.4. Conductivity recorded by FRA system, temperature 297 K. Plot 1-0.1V AC ,0 bias, plot 2-0.1 V AC 9.9V bias.

One may observe increasing value of DC-like conduction. On other hand , in Fig 4 the result of FD experiment is displayed. The experiment consisted of recording of sample conductivity and capacitance in biased sample. As one can see, the results are incompatible. The conductivity of biased sample is smaller than for non-biased one. The same discrepancy is for the case of sample capacitance value.

It is the proof that TD and FD technique are recording, in nonlinear samples, different properties. Therefore particular statement based on FD measurements may not be true unless the linearity of the system is not verified. DC like conduction at elevated time was observed in liquid crystals so far [2]. The basic problem is hidden not in DC like conduction in PCB, but in apparent absence of recombination process in space charge layer.

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DIELECTRIC PROPERTIES OF POLYETHYLENE MODIFIED BY MONOESTERS OF MALEIC ACID

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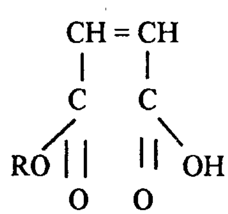
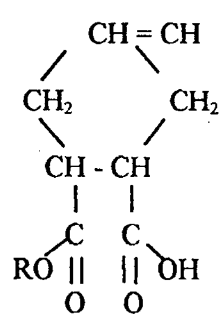
Introduction

New group of coagents, which were used as modifiers of low density

polyethylene (LDPE), has been synthesized. The coagents increases efficiency of crosslinking reaction and improve mechanical properties of the polymer. Substances with different molecular size and especially structure of substituent belong to this group. We were particularly interested in monoesters of maleic acid and their derivatives of the following formulas:





where: $R=C_3H_5$ (A)
$R=C_3H_5$ (TH)
$R=C_4H_9$ (B)
$R=C_{12}H_{25}$ (D)

A mobility of the coagents molecules in the polymer matrix is of special interest because they could interact with macromolecules of LDPE influencing their ability to crystallization and take part in reactions with polymer macromolecules initiated by organic peroxide. After grafting the carboxyl group of the coagents was utilized to form in reaction with metal oxides e.g. ZnO, aggregative crosslinks of cluster type. An effect of the coagents on crosslinking of LDPE, a degree of its crystallinity and mechanical properties have been published in [1].

Now we try, using the dielectric analysis, to obtain additional information about molecular motion of modifiers and their influence on LDPE.

Object of investigations

Low density polyethylene (MALEN E - PETROCHEMIA PŁOCK) was chosen for the study. Allyl maleate (AM), butyl maleate (BM), dodecyl maleate (DM), allil tetrahydrophtalate (THFA) synthesized from maleic anhydride and appropriate alcohols, were used as modifiers. The modifier content was equal to 10 mmoles per 100 g of LDPE.

Compounds were prepared by means of Brabender Plasti-Corder apparatus at the temperature 428 K. At this stage organic peroxide and metal oxides have not been added.

Tab. 1. Composition of compounds

Symbol	Composition of compounds	Weight part [g]
PE	LDPE	100
A	LDPE/AM	1,6
B	LDPE/BM	1,8
D	LDPE/DM	2,9
TH	LDPE/THFA	2,1

Results

The measurements were carried out in the air in the frequency range 10^{-2} Hz $\div 10^{4}$ Hz with Solartron 1250 Frequency Response Analyser +Chelsea Dielectric Interface. rms ac of the measuring signal was equal 1 V, no external DC voltage was applied. The temperature range used was 293 K up to 363 K.

The dielectric properties of A, B and TH samples turns out to differ significantly from the dielectric properties of the D sample.

The first three samples proved to be typical low-loss materials with practically frequency independent real part of dielectric permittivity and tan 8 in the range between $10^{-3} \div 10^{-2}$.

The dielectric response of the D sample may be well described with the expression:

$$\varepsilon(\omega) = A_h(i\omega)^{n-1} + B_1(i\omega)^{m-1}$$

where n describes the frequency dependence of the high-frequency part of the permittivity and m is responsible for the low-frequency part of the response. n is close to unity in the whole temperature range used while m changes from about 0.3 for the lower temperatures to about 0.1 for the higher temperatures. A detectable (by about 0.5 order of magnitude) inerease in the real part of permittivity has been detected. It may be supposed that the detected increase in the dielectric losses below about 100 Hz may be either due to molecular movement of polar modifier or due to increased degree of crystallinity of the polyethylene matrix. It has been suggested [1] that the D-modifier may give rise to increase in the degree of crystallinity of the matrix, so the second supposition seems to be in agreement with the previously obtained results. Further investigations are in process in order to describe the influence of the modifers used on the molecular structure of the modified polyethylene

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TUNNELLING-MEDIATED RECOMBINATION-INDUCED LUMINESCENCE IN POLYETHYLENE NAPHTHALATE

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Electroluminescence in insulating polymers can be addressed on two standpoints : the excitation mechanism, i.e. the way in which excited states of molecules are being produced, and the relaxation mechanism, i.e. the pathway along which molecules return to their ground state. The excitation step may be achieved in different situations :

i/ band to band recombination, which is unlikely in insulating polymers for the band gap is too large,

ii/ impact excitation or ionisation, which means that collisions between hot electrons and the medium bring the molecule to an excited state or either ionise it. For dissociative collisions, an excited state is produced via the recombination of ion pairs.

iii/ of chemical nature : the excited state may result from the creation of new chemical species in the material. The new function would be created in the excited state, the chemical reaction being initiated by mechanisms such as *ii/*.

Polyethylene Naphthalate -PEN- belongs to the class of polymers in which chromophores - i.e. light emitting groups are present in the repeat unit of the polymeric chain (Fig. 1), as opposed to polyolefins as example whose chromophores are necessarily unsa-turations, i.e. chemical defects of the structure. Evidence has been given that the field threshold for electro-luminescence -EL- emission under DC stress is correlated to the onset of high mobility regime of conduction [1]. Hence, mechanisms *ii/* are believed to be the dominant excitation path for PEN, at least at moderate field. Process *iii/* seems to occur as field further increases since a component of the EL spectrum not originally present in the photoluminescence -PL- emission spectrum appears and strengthens.

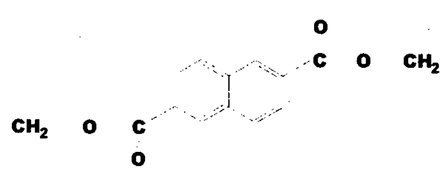

Figure 1. The repeat unit of PEN.

Our concern in this work is to pursue the interpretation of EL in PEN on the basis of hypotheses *ii/*. If EL originates from impact excitation, one would expect that the light emission after stress (field) removal decay at a rate corresponding to the natural lifetime of the excited states, which are predominantly triplet states in the present situation. This is indeed not the case since EL could be recorded for about 200 s at room temperature -RT- (see fig. 2) while the natural lifetime of triplet states is of the order of some ms at liquid nitrogen temperature (LNT). Besides, we have shown that in the whole time range of measurement, the decay can be fitted by a law of the form:

$$I = Io.[1+\alpha.t]^{-m} \qquad (1)$$

Such a decay law has often been interpreted as radiative recombination whose kinetics is controlled by the tunnelling rate of an electron trapped in the neighbourhood of its parent cation to this cation. An analytical form of the distribution of electron-cation separation distances can be deduced from eq. 1. This decay law has been found for a variety of ionising sources, being UV, g-, or X-ray [2, 3], though it is to our knowledge the first report on its applicability to electroluminescence. Further support to tunnelling-assisted recombination arises from the observation that the kinetics is essentially the same at RT and LNT. Besides, the use of an alternative excitation source, which was ambipolar charging by a cold plasma in inert atmosphere, lead to the same decay kinetics.

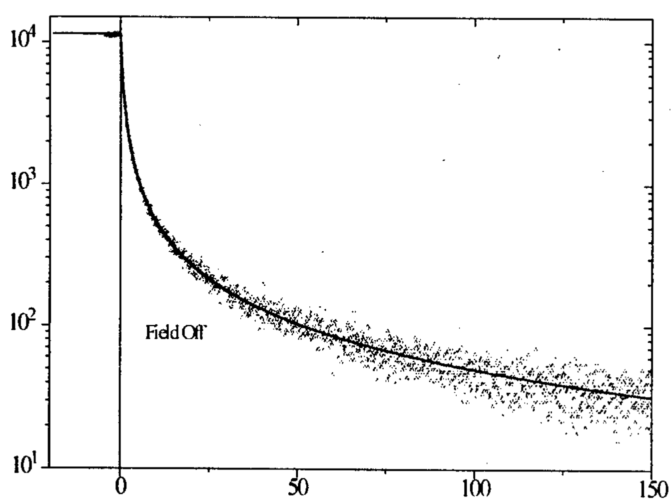

Figure 2. Decay of EL following excitation at RT : E = 3.1 MV/cm. Fit parameters : a = 1.63 s⁻¹; m = 1.067.

The emission spectra for the different excitations, namely EL, PL and plasma-induced luminescence had quite different shape though they all displayed the phosphorescence of PEN. An energy diagram describing the tunnelling recombination mechanism could be drawn on the basis of the energy diagram of the monomeric unit of PEN on one hand, and of the differences found between EL and PL spectra on the other.

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ON DETERMINATION OF THE TRAP DISTRIBUTION IN DISORDERED SOLIDS FROM THE FINAL DECAY OF TRANSIENT PHOTOCURRENTS

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The investigations of transient photoconductivity of disordered solids provide useful information about the energy distribution of localized states (traps) in the forbidden gap. Two basic techniques can be distinguished, that is the time-of-flight (TOF) and the transient photocurrent (TPC) experiments (see, e.g. the review [1]). In both cases, several methods of determining the distribution of trapping states in a solid had been developed. In particular, Senhaeve *et al* [2] have utilized for this purpose the final decay of photocurrents, measured in the TOF experiment. The method seems to be very reliable, since the long-time behaviour of the photocurrent is independent of many physical factors such as the non-uniform spatial distribution of the electric field or the trapping states.

Some deficiency of the mentioned method is relatively low energy resolution, of the order of $3kT$ (k - Boltzmann constant, T - sample temperature). This is of significance when the trap density exhibits sharp peaks, due to the dangling bonds or the other defects. Therefore, it is desirable to develop the more accurate methods of analysis of the final photocurrent decay. This is the purpose of the present communication.

According to [2], the asymptotic behaviour of the photocurrent $I(t)$, measured in the TOF configuration, is given by

$$I(t) \approx \frac{I_0 \tau_0^2 C_t}{2} \int_{\varepsilon_t^0}^{\varepsilon_t} N_t(\varepsilon) \tau_r^{-1}(\varepsilon) \exp\left[-t/\tau_r(\varepsilon)\right] \mathrm{d}\varepsilon, \quad t >> \tau_e. \tag{1}$$

Here, t and ε are the time and energy variables, respectively, I_0 is the initial photocurrent intensity, τ_0 is the free carrier time-of-flight, C_t is the carrier capture coefficient, $N_t(\varepsilon)$ is the trap density, $\tau_r(\varepsilon) = \nu_0^{-1}\exp(\varepsilon/kT)$ is the mean carrier dwell-time in the trap (with ν_0 the frequency factor), ε_t^0 and ε_t are the limits of trap distribution and τ_e is the effective carrier time-of-flight. Similar formula describes the photocurrent obtained in the TPC configuration, for the time much longer than the mean time of carrier recombination [3].

In [2] the integral equation (1) for $N_t(\varepsilon)$ was approximately solved by replacing the product of the second and third terms in the integrand by the Dirac delta function. However, analogous approach may be also applied to the time derivatives of $I(t)$:

$$\frac{\mathrm{d}^m I(t)}{\mathrm{d}t^m} \approx \frac{(-1)^m I_0 \tau_0^2 C_t}{2} \int_{\varepsilon_t^0}^{\varepsilon_t} N_t(\varepsilon) \tau_r^{-(m+1)}(\varepsilon) \exp[-t/\tau_r(\varepsilon)] \, \mathrm{d}\varepsilon, \quad t >> \tau_e, \qquad (2)$$

and the corresponding function in the integrand approximates more exactly the delta function. In this way one obtains the formulae

$$\tau_r^{-(m+1)}(\varepsilon) \exp[-t/\tau_r(\varepsilon)] \approx m! t^{-(m+1)} kT \delta[\varepsilon - \varepsilon_m(t)], \qquad (3)$$

$$\varepsilon_m(t) = kT \ln[\nu_0 t/(m+1)] \qquad (4)$$

(with $\delta(\ldots)$ the delta function) and, in consequence,

$$N_t[\varepsilon_m(t)] \approx \frac{(-1)^m t^{m+1}}{m! c_0 I_0 kT} \frac{\mathrm{d}^m I(t)}{\mathrm{d}t^m}, \quad \varepsilon_t^0 < \varepsilon_m(t) < \varepsilon_t. \qquad (5)$$

In the case of $m = 0$ (no time derivative of the current) the above formula reduces to that derived in [2].

The accuracy of Eq. (5) has been checked by using the model trap distribution, similar to that utilized in [2]. In this model, the trap density is represented by the linear combination of exponential and Gaussian functions:

$$N_t(\varepsilon) = N_{tot} \left\{ \frac{(1-r)}{kT_{c1}} \exp\left(-\frac{\varepsilon}{kT_{c1}}\right) + \frac{r}{\sqrt{\pi}\, kT_{c2}} \exp\left[-\left(\frac{\varepsilon - \varepsilon_{t2}}{kT_{c2}}\right)^2\right] \right\}. \qquad (6)$$

Here, N_{tot} is the total trap density and the remaining parameters characterize the shape of trap distribution. The current $I(t)$ has been initially calculated from Eqs.(1) and (6) and then the trap distribution $N_t(\varepsilon)$ has been obtained via Eq.(5). The results of calculations are shown in Fig. 1. It is seen that the accuracy of Eq. (5) ameliorates with increasing m, which proves the potential usefulness of the proposed method. The initial discrepancies have no practical significance, since the corresponding time region is not accesible experimentally.

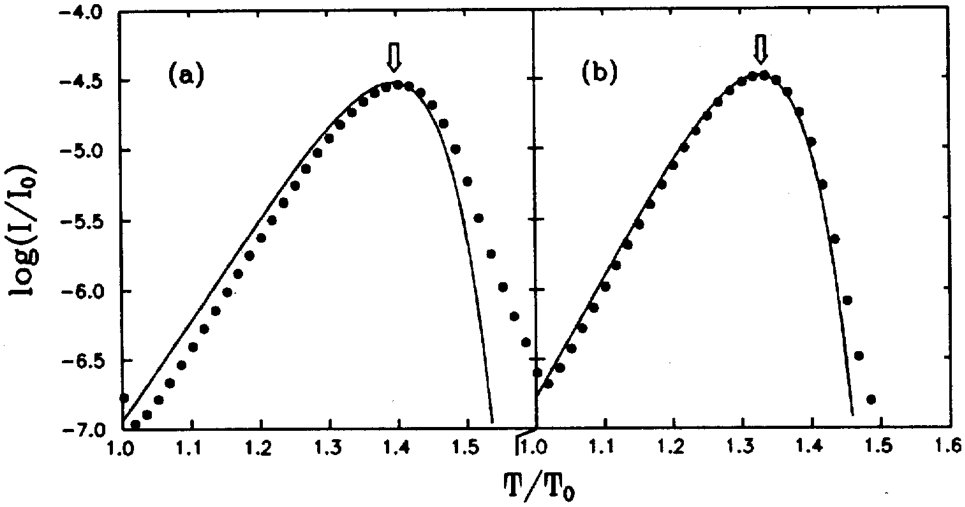

Figure 1. Calculated current transient (a) as well as input (points) and output (lines) trap distributions (b). The parameters: $r=10^{-4}$, $T_{c1}=1.25T$, $T_{c2}=2T$, $\varepsilon_{t2}=25kT$, $\tau_0^2C_t=2/\nu_0N_{tot}$.

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ON THERMALLY STIMULATED CURRENTS UNDER QUASI-EQUILIBRIUM TRANSPORT REGIME

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The characteristic feature of disordered solids is the continous distribution of trapping states located in the energy gap. In the description of thermally stimulated currents (TSCs) in these materials one has to take into account the processes of carrier trapping/detrapping for arbitrary trap depth as well as of the carrier recombination. This may be done solely in the approximate way and different approaches have been used in the previous papers on the subject. In particular, in [1,2] the strongly non-equilibrium trapped carrier distribution has been assumed.

In the present communication the formulae for TSCs are derived under the another assumption, i.e. the approximate thermal equilibrium between the free and trapped carriers. This is the case of the energetic trap density $N_t(\varepsilon)$ decreasing relatively fast with the energy ε (measured from the edge of allowed band). Then, the carrier trapping/detrapping kinetics is described by

$$n_t(t) = \frac{1-\Theta(t)}{\Theta(t)} n(t) \tag{1}$$

(with t the time, $n(t)$ and) $n_t(t)$ the free and trapped carrier densities). The function $\Theta(t)$ is given by

$$\Theta^{-1}(t) = 1 + C_t \int_{\varepsilon_t^0}^{\varepsilon_0(t)} N_t(\varepsilon)\tau_r(\varepsilon,t)\,\mathrm{d}\varepsilon\,, \tag{2}$$

where C_t is the carrier capture coefficient, $\tau_r(\varepsilon,t) = \nu_0^{-1}\exp[\varepsilon/kT(t)]$ is the mean carrier release time (ν_0 - the frequency factor, k - the Boltzmann constant, $T(t)$ - the sample temperature), $\varepsilon_0(t)$ is the demarcation energy level (c.f. [2]) and ε_t^0 is the lower trap distribution limit. The monomolecular and bimolecular recombination of carriers is described by

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[n(t) + n_t(t)\right] = -\frac{n(t)}{\tau_R}\,, \tag{3}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[n(t) + n_t(t)\right] = -C_R n(t)\left[n(t) + n_t(t)\right], \tag{4}$$

respectively, where τ_R and C_R denote the mean carrier recombination time and the carrier recombination coefficient. As an exemplary trap distribution the exponential one is choosen

$$N_t(\varepsilon) = \frac{N_{tot}}{kT_c}\exp\left(-\frac{\varepsilon-\varepsilon_t^0}{kT_c}\right), \quad \varepsilon \ge \varepsilon_t^0 \tag{5}$$

(with N_{tot} the total trap density, T_c the characteristic temperature).

Solving Eqs.(1) and (3) as well as Eqs.(1) and (4) one obtains the following formulae describing TSCs:

$$I(t) = I_0\Theta(t)\exp\left[-\frac{1}{\tau_R}\int_0^t \Theta(t')\,\mathrm{d}t'\right] \tag{6}$$

(the monomolecular recombination case) and

$$I(t) = \frac{I_0\Theta(t)}{1 + C_R n_0 \int_0^t \Theta(t')\,\mathrm{d}t'} \tag{7}$$

(the bimolecular recombination case). Here, n_0 denotes the initial trapped carrier density, $I_0 = en_0\mu_0 ES$, where e is the elementary charge, μ_0 is the free carrier mobility, E is the field strength and S is the sample cross-section area.

The accuracy of above formulae has been verified by solving numerically the sets of Eqs.(1) and (3) as well as of Eqs.(1) and (4) with the use of Gear's algorithm [3]. The comparison of the exemplary analytical and numerical results is presented in Fig.1.

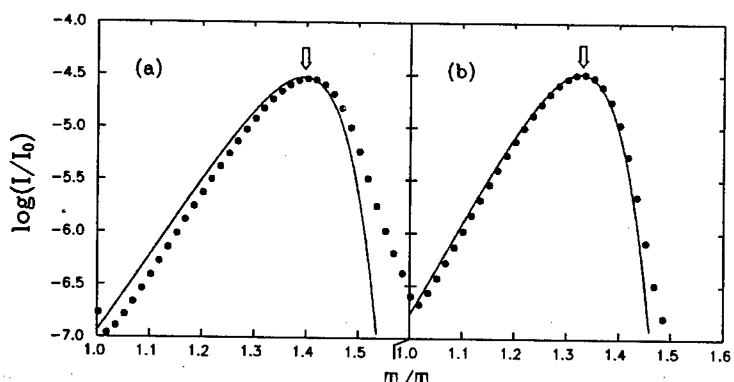

Fig. 1. TSC curves calculated for exponential trap distribution with two different values of T_c and monomolecular recombination. The points are numerical results, the solid lines correspond to Eq. (6). The parameters: $\tau_t\nu_0 = 10^5$ (τ_t - the mean carrier trapping time); $\tau_R\nu_0 = 5\times10^9$; $\beta/\nu_0 T_0 = 10^{-15}$ (β - the heating rate, T_0 - the initial sample temperature); $T_c/T_0 = 1.5$ (a), 1.2 (b); $\varepsilon_t^0/kT_0 = 25$; $T_0 = 100$K.

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DIELECTRIC PROPERTIES OF COMPOSITE STRUCTURES WITH DIFFERENT TWO DIMENSIONAL NETWORKS

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Heterogeneous systems composed of two or more phases show different conductive and dielectric properties depending on electrical properties of the phases[1]. Since such systems are playing an important role in modern insulation technology, there is a need to predict their dielectric properties. In this study, computations of frequency dependent dielectric properties of a two phase system composed of conductive cylindrical rods in a less conductive matrix are presented. The rods were distributed on regular i.e. square(sq), honeycomb(hc) and hexagonal(he), and random networks. The effective medium approach was applied. Each of the networks has its limiting concentration (q_{sq}= 0.7854, q_{hc}= 0.6046 and q_{he}= 0.9069). An unit cell, which was the smallest repeatable part of the whole network, was taken into account. Frequency dependent dielectric constants of the networks were computed using finite element method[2]. The permittivities of the rods and matrix were both equal to 4, and the conductivities were $1\mathrm{x}10^{-7}$ and $1\mathrm{x}10^{-20}$ $(\Omega\mathrm{m})^{-1}$, respectively. An increase in concentration of the rods was followed by an increase in the dielectric constant at the low frequency side. However, the increase was not the same for the networks even though they had the same concentration. This phenomenon could be explained by the interaction of the inclusions with each other. In addition, hypothetical thermally stimulated depolarization current spectra were also computed for the networks, based on the classical model[3]. We concluded that it is possible to have the same dielectric response from a composite with lower concentrations of conductive inclusions providing they are appropriately distributed in the matrix.

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CIRCUIT INFLUENCE ON POLARIZATION REVERSAL IN $BaTiO_3$ CERAMICS

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The polarisation switching properties of a ferroelectric are usually studied using an RC circuit in which C is a non-linear capacitor made of the material under investigation. For a long time, the parameters of the recorded switching current were considered as characteristics of the ferroelectric material existing inside the capacitor C, and the research efforts aimed to correlate them with the structural characteristics. However, studies performed by Larsen [1] proved that in case of PZT ferroelectric thin films, decreasing the values of C in the measurement circuit determines the decrease of the switching time, but no lower limit could be observed.

We considered that the recorded voltage profiles on the series resistor R of a non-linear RC circuit, characterises the entire circuit, not only the polarisation reversal process inside the ferroelectric. Under this hypothesis, we investigated the influence of the RC circuit parameters on the results of polarisation switching experiments performed on ferroelectric $BaTiO_3$ ceramic samples with 500 nm grain-size. We tried to find a lower limit of the switching time as a characteristic of barium titanate, irrespective to the measurement circuit.

The ceramic samples investigated in our study were prepared in a multilayer technology, using a fme barium titanate powder with 50 nm grain-size. Details of preparation are given in a previous work [2]. The ceramic capacitors used in the switching experiment were obtained an the same ceramic disk, by applying silver paste electrodes of different areas. Two capacitors with $C_M = 2.5$ nF and $C_m = 50$ pF, were consequently connected with series resistors of $R_M = 1$ MΩ and $R_m = 50$ Ω, in order to obtain RC series circuits with different parameters. Electric field pulses of 4 MV/m were applied using a circuit comprising two dc voltage supplies and three mercury relays. The transient voltage on the series resistor R was recorded using a computer-controlled oscilloscope.

The switching currents recorded in these four circuits are presented in Fig. l. It can be seen that decreasing the values of R , C or both, the switching time decreases. The profiles of switching currents exhibit major changes when changing the parameters of the RC circuit, even the capacitors are build on the same ceramic plate. These results led us to the conclusion that the observed changes of the switching time or switching current profile are consequences of the fact that, during polarisation reversal, the ferroelectric is under the influence of an electric field whose shape is much different from a rectangle. The real shape is complicated and dependent on the values of R and C. In order to obtain information relative to the investigated material only, an appropriate model of the ferroelectric material is needed. The switching characteristics of a ferroelectric material cannot be found directly from polarisation reversal experiments. This characterisation is possible only by model parameters found by numerically solving the differential equation of the RC non-linear circuit.

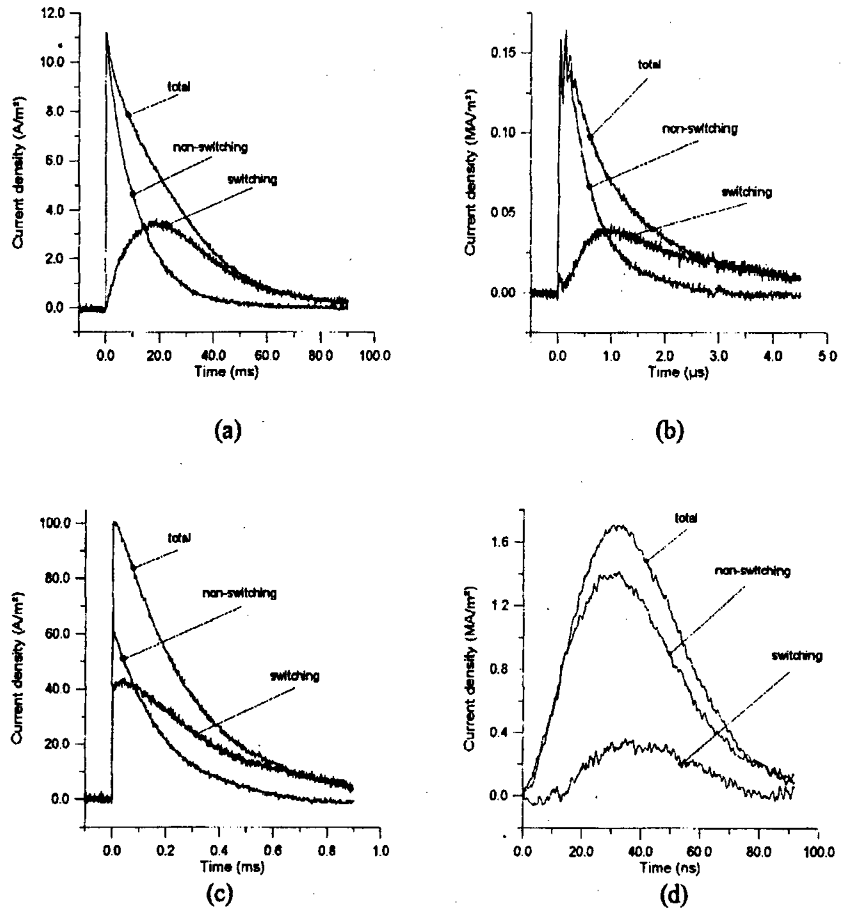

Fig. 1 Total, non-switching and switching current profiles determined by electric field pulses of 4MV/m, recorded in RC non-linear circuits with the following parameters: (a) $C_M = 2.5$ nF , $R_M = 1$ MΩ ; (b) $C_M = 2.5$ nF , $R_m = 50$ SZ ; (c) $C_m = 50$ pF , $R_M = 1$ MΩ ; (d) $C_m = 50$ pF , $R_m = 50$ S2 .

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MOLECULAR DIPOLE MOMENTS DETERMINED FROM DIELETRIC MEASUREMENTS IN VERY DILUTED SOLUTIONS

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Dielectric measurements have been performed for more than twenty dipolar liquids in non-polar solvents and their dipole moments have been calculated using the formula given by Makosz [1] and basing on the Onsager theory with Scholte's [2-4] correction for an
ellipsoidal shape of dipole molecules.

$$\mu_1^2 = \frac{a_2^3 KT(2\varepsilon_1+1)}{3\varepsilon_1^2[\varepsilon_1+(1-\varepsilon_1)A_0]}\left[\frac{\varepsilon_1+(\varepsilon_2^\infty-\varepsilon_1)A_0}{1+(\varepsilon_2^\infty-1)A_0}\right]^2\left[\frac{3\varepsilon_1}{(2\varepsilon_1+1)}\left(\frac{\Delta\varepsilon}{\varphi_2}\right)_{\varphi_2\to 0}-\frac{3\varepsilon_1(\varepsilon_2^\infty-\varepsilon_1)}{2\varepsilon_1+\varepsilon_1^\infty}\right]$$

The results obtained for dipolar liquids under study (from small dipole moment: toluene, o-xylene, trichloroethylene, 1,2-dibromoethane, 1,2-dichloroethane, aniline, dibromomethane, 1-butanol, dichloromethane, iodomethane, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, ethyl alcohol, ethyl acetate, o-chlorophenol, acetone, 1-nitropropane, benzonitrile, nitrobenzene) for two temperatures, 25 and 50 °C, and for a few solvents (CCl_4, $C_4H_8O_2$, C_5H_{12}, C_6H_6, C_6H_{12}, C_6H_{14}, $C_{16}H_{34}$) are presented.

The obtained values of dipole moments are in good agreement with those measured for molecules in the gaseous state. For comparison, the values of the dipole moments calculated according to other formulae from early papers are given [5].

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CHARGE SEPARATION AND RECOMBINATION IN SENSITIZED PHOTOCONDUCTING POLYIMERS

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Sensitized polymers, for instance, such as poly-N-vinylcarbazole (PVCz) or poly-N-epoxypropylcarbazole (PEPCz) are promising photoconductive materials and are already extensively employed in electrophotography for production of organic flexible electrophotographic layers. According to the spectroscopic data, the sensitizing molecules form complexes with the neighboring carbazolyls of the polymer and a few types of optically observable charge transfer (CT) states. Complex excitation results in efficient charge separation leading to charge carrier production. Discussion of the mechanisms of a fast and effective charge separation and the subsequent slow geminate recombination is the subject of the given report.

Time resolved absorption and fluorescence spectroscopy and MonteCarlo simulations were employed for investigation of the charge. separation and recombination dynamics in films and solutions of PEPCz sensitized with 2,4,7-trinitro-9-fluorenone (TNF) forming a weak ground state CT- complex with electron-donating carbazolyl radical. Dynamics of carbazolyl cation radical absorption and its polarization was measured with picosecond and femtosecond resolution and charge recombination dynamics on a nanosecond time scale was measured by time-correlated single photon counting technique.

Very fast (subpicosecond) hole transfer over several carbazolyl moieties in PEPCz films was concluded from a very fast loss of carbazolyl absorption polarization memory. The primary charge separation efficiency was determined to be about 70-80%. The geminate recombination of an electron-hole pair is nonexponential and much slower extending into nanosecond time domain. The dependence of the primary charge pair separation efficiency and distance on the excitation wavelength and on the acceptor concentration is concluded from recombination dynamics. Comparison of experimental data with results of Monte-Carlo simulations enabled to determine the mean distance and distribution of initially separated charge pairs. Simulations also revealed importance of energetic and positional polymer disorder for charge pair separation and recombination processes.

It is suggested that the difference in electronic polarization in the initial CT-state and in the final state of separated charges creates the driving force of the photogeneration process. The model based on this suggestion assumes that the hole transfer from the CT-states to the neighboring carbazolyl radicals can be considered as a dynamic process stimulated by such difference in electronic polarization, while afterwards a stochastic reorganization of the surrounding has also to be taken into account. Consequently, the geminate recombination is considered as a random walk of the hole over the spectrally disordered landscape of the relaxed polymer molecules. The initial reorganization of the surrounding is defmed by means of the Fokker-Planck equation which determines the evolution of the probability for the separated charges in the configuration space coordinate.

TESTING OF MECHANICAL PROPERTIES OF MATERIALS BY MEANS OF OPTICAL METHOD

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Optical method making use of diffraction of the light of the laser on optical slit [1-3] has been applied to investigate of mechanical properties of materials. Schematic view of measuring system is shown in Fig.1.

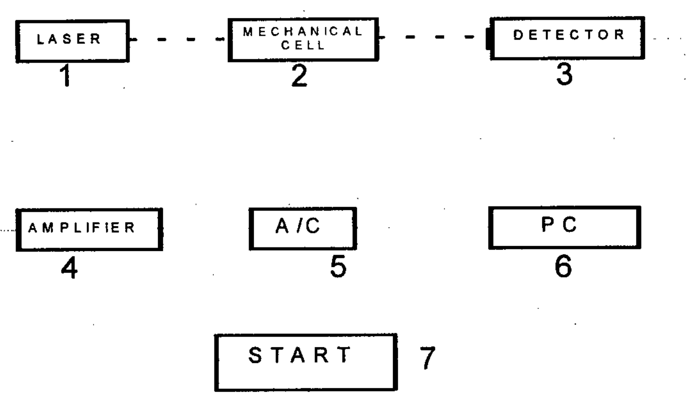

Fig. 1. Block presentation of measuring system. 1 - He-Ne laser, 2 - cell for mechanical measurement, 3 - detector, 4 - amplifier, 5 - 12 bit A/C converter, 6 - computer, 7 -"start" button and delay line

Detector consist of BPW 34 fotodiode. Delay line is used for adjustment of the time of mechanical pulse and start of the system of recording of optical signal. Cell used for mechanical measurements is shown in Fig.2.
As shown in Fig.3. metal ball 5 strike bar 1 thus exciting bar oscillations. Oscillating bar changes slit 3. The width of the slit 3 is recorded by means of optical system. Optical signal is transformed by the fotodiode to electrical one, thus amplified and digitalised. In one experiment is recorded up to 8000 measurement points. The records were stored in computer memory. Then damped wave form g(t) was fitted to experimental data Y(t) by means of last square method. The example of such fit is shown in Fig.3.

In numerous materials (Al, glass, plastic materials - hostaform, bakelite) there exist stable frequency of oscillations and the decay of amplitude is exponential. However in particular materials (ceramic, polypropylene with 40% of chalk) the frequency of oscillations is not stable as well as there are deviations from exponential decay of the amplitude of oscillations.

There is an attempt of the use of the methods to investigate mechanical properties of fibbers.

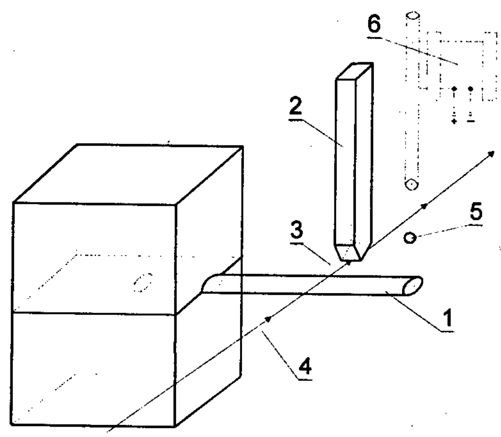

Fig. 2. Schematic view of setup used for transformation of mechanical values into optical signal.

1 - bar-shaped material subjected to mechanical oscillations, 2 - edge for adjustment the slit 3, 3 - slit, 4 - laser beam, 5 - metal ball, 6 - metal ball injector.

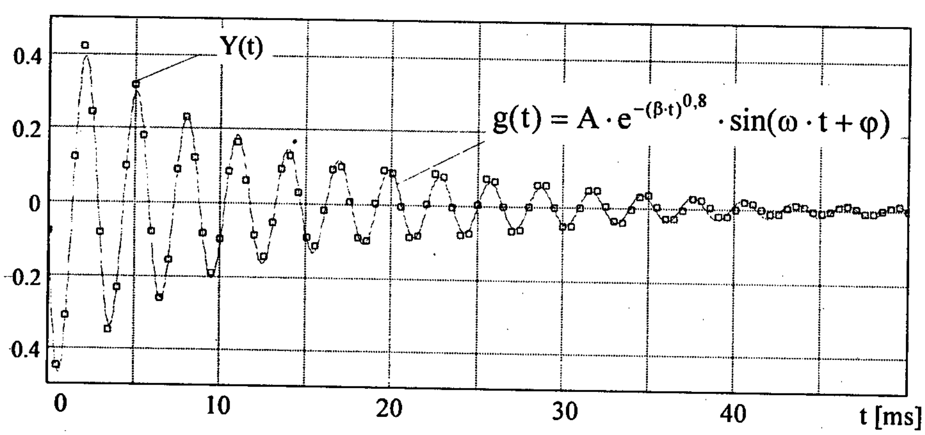

Fig. 3. Amplitude as a function time.

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METAL/INSULATOR CONTACTS IN ELECTRICAL EXAMINATIONS OF $M/Yb_2O_3/M$ THIN-FILM STRUCTURES

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An experimental study of current-voltage characteristics for metal/ytterbium oxide/metal samples is presented. $M/Yb_2O_3/M$ thin-film sandwiches (where M≡different metal electrode) were fabricated by vacuum deposition method. Electron-gun assisted deposition as well as thermal oxidation techniques were applied for preparation of the insulator film.

The current-voltage characteristics follow $I=AU^n$ relationship (with n in the range from 1 to 14). For the positive and negative voltage bias I=I(U) curves exhibit the assymetry up to 5 decades values of the current. Electrical properties of $M/Yb_2O_3/M$ structures were discussed taking into account ohmic and blocking contacts at metal/insulator boundaries. It was shown that Schottky barriers formed at M/I interfaces are very important in electrical examinations of these structures. The influence of these barriers is also well seen in examinations of dielectric response of $M/Yb_2O_3/M$ structures (non-steady-state I=I(t) characteristics and alternating current response studies).

ELECTRICAL PROPERTIES OF SOME PLASMA POLYMERS OBTAINED BY REMOTE MICROWAVE PLASMA CHEMICAL VAPOUR DEPOSITION

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Amorphous hydrogenated silicon-carbon (a-Si:C:H) films were produced by remote microwave hydrogen plasma chemical vapour deposition (RHP-CVD) technique using trimethylsilane (films obtained indicated with TrMS) and pentamethyldisilamethanc (films obtained indicated with PMDSM) as single-source precursors [1]. The films were deposited onto crystalline n-type silicon substrates heated at various tempcratures. The films provided with metal Au/A1 electrodes were also obtained.

Some electrical properties of Al/TrMS/Au structures (TrMs sample 100nm thick) were measured. The DC conduction has been measured at various temperatures (Fig. 1.). The conductivity below about 10^6 V/m was nearly ohmic, the activation energy being about 0.29eV. The dielectric response is due to DC conduction below 100 Hz. Above 100 Hz the response is typical of low-loss materials with tan 8 smaller than 0.01 .

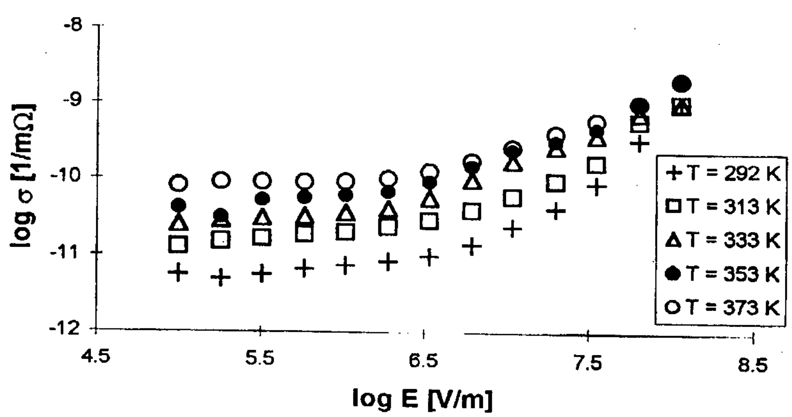

Fig.l. DC conductivity ofAllTrMSlAu system at various temperatures,.

The electrical properties of M1S structures with TrMS as an insulating film was also measured. The current-voltage characteristics are strongly asyminetric. A narrow ohimc region for the small polarisation n-Si(+)AI(-) has been detected. The activation energy for these voltages equals about 0.55 eV. The dielectric response of the Al/TrMS/n-Si structures shows two relaxation processes at the peak frequency equal to about 0.5 Hz and 20 Hz. The capacitance-voltage curves (Fig.2.) are typical for real M1S structures with measurable concentration of electronic states at the insulator/semiconductor interface [2,3]. The density of the traps per unit surface area was estimated to be about $8 \cdot 10^{15}$ eV^{-1} m^{-2}[4].

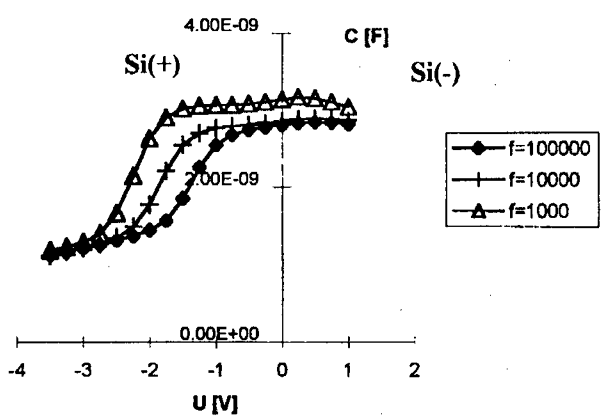

Fig.2. Capacitance-voltage characteristics of Al/Tr-MS/n-Si system at room temperature.

The electric properties of MIS structures with PMDSM filrns on n-type silicon substrates are different from those of Al/TrMS/n-Si films. The current values at the opposite values of the voltage are close to each other. At the polarisation Si(-)Al(+) the current-voltage dependence proves to be linear with the activation energy between 0.30-0.34eV depending on the voltage. The dielectric response of the MIS structure shows one relaxation process at the peak frequency close to 150 Hz.

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DIELECTRIC PROPERTIES OF LIQUID CRYSTALLINE S-MHPOBC IN THE RANGE OF LOW-FREQUENCIES

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MHPOBC is a well known liquid crystalline (LC) compound in which the antiferroelectricity has been discovered [1]. The following phases has been detected in this material: smectic A, ferroelectric SmC*, ferrielectric and two types of antiferroelectric SmC^*_A and SmI^*_A [2]. The main aim of the presented research was to find the relation between the various LC phases and the dielectric response of S-MHPOBC in the low-frequency range.

The S-MHPOBC was sandwiched between two glass plates covered with ITO electrodes separated by 5 wm thick spacer. The thickness of the sample was comparatively small which may give rise to some shift down of the phase transition temperatures [3].The planar arrangement of the system was obtained. The dielectric measurements were carried out using Solartron 1260A Impedance Analyser with Che]sea Dielectric Interface. The measuring rms ac voltage was equal to 0.1 V. The DC bias in the voltage range 0 –l0V DC was also applied. The measurements were carried out in the frequency range from 10^{-4}Hz up to $5*10^4$Hz. The accuracy oftemperature control was better than 0.02 K. Both real and imaginary part of electrical capacitance were obtained as a result of the measurements. The results were elaborated with WinFIT software assuming the validity of Havriliak-Negami equation for the loss peaks registered.

Two loss peaks in the frequency range used have been detected. The maximum of the first one was between 0.1Hz and 10 Hz in the temperature range used. The maximum of the second peak was about l OkHz in the temperature range corresponding to ferro- and ferrielectric phases.This peak is characteristic of ferroelectric liquid crystals and has been recognised as a so-called Goldstone mode [4,5]. The activation energy of the first peak equals 0.90 eV in the whole temperature range used, the activation energy of the second one is lower and equal to 0.59 eV.

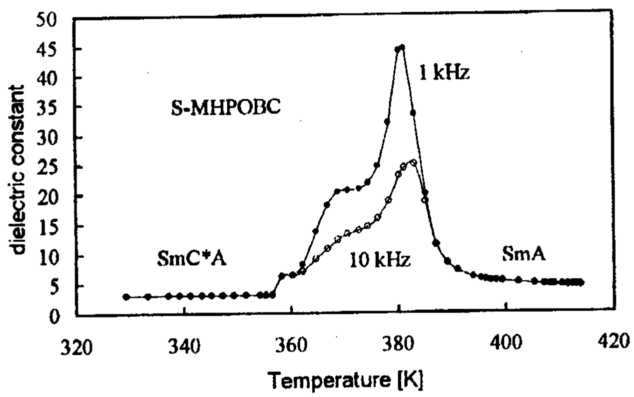

Fig.1 Temperature dependence of the dielectric constant, for S MHPOBC 5 m thick sample at two various frequencies .rms ac=0. I hdc voltage-Oh The measurements were carried nut during a enoling cycle.

For the first peak the maximum value of the dielectric permittivity is in principle independent of the voltage, for the secorid one the maximum value decreases with increasing voltage in the voltage range 0÷10V. The temperature dependence of dielectric permittivity enables to determine the phase sequence for the investigated material. The ferroelectric phase may be also determined from the temperature dependence of the dielectric strength of both peaks and from the slope of the high-frequency side of the first low-fi-equency peak. The transition temperature between antiferroelektric and ferrielectric phase may be also determined from the temperature dependence of the slope of both sides of the first low-frequency peak.

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DETERMINATION OF THE SPLAY AND BEND ELASTIC CONSTANTS FOR THIN NEMATIC PLANAR LAYER IN EXTERNAL ELECTRIC FIELD

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Elasticity is a fundamental criteria for application capability of nematic liquid crystals. The basic difference between deformations in liquid crystals and in a solid is that in liquid. crystals there is no translational displacement of the molecules in distortied sample. Th.e elasticity of a solid is related to the changes in density. In liquid crystals, variations in density can also be characterised by a suitable modulus, but the elasticity is related to the local variation in the orientation of the director.

From dielectric investigation of Frederics transition for planar nematic layer of 6-CHBT placed in high electric field the splay and bend elastic constant have been determined. The dependence of capacity change of investigated nematic layer on the intensity of external electric field own threshold eharacter. From values of threshold fields we determined the splay (K_1) elastic constant. The bend elastic constant (K_3) have been determined from the extrapolated procedure for the high electric field region (where we observed the saturation effect). From this experiment the dielectric properties of investigated nematics have been determined (the anisotropy of electric permitivity and perpendicular component of its tensor). Results obtained using described method agree well with literature data.

DIPOLE-DIPOLE CORRELATION AND ODD-EVEN EFFECT IN HOMOLOGOUS SERIES OF BICYCLO-[2,2,2] OCTANES DERIVATIVES WITH -NCS TERMINAL GROUP

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Short range dipolar interactions play a significant role in liquid crystal phases. Molecular association is one of the dipolar forces manifestations, which results is an antiparallel agregation of molecules. The dipol-dipol interaction together with presence of the flexible aliphatic chain attached to the rigid rod-like molecules are essential for stabilisation of nematic phase. Most physical quantities of liquid crystals show a characteristic alternation as a function of the number of the aliphatic chain segments (the odd-even effect). One of this quantities is the electric permitivity. In this paper the static electric permitivity measurements of homologous series of bicyclo-[2,2,2]octanes derivatives with NCS terminal group are presented. Permitivity have been measured as a function of temperature in the isotropic and the nematic phases. The main moment components along principial direction of liquid crystals of the square effective dipol have been determined from Maier-Meier equations. The order parameter data needed for this calculation were obtained from birefringence measurements. Within the studied series the Kirkwood correlation factor exhibit the odd-even alternation. The correlation factor have been interpreted in terms of an anti-parallel association. This association have been confirmed in dielectric measurements of bicyclo-[2,2,2] octanes derivatives with -NCS terminal group in dilute benzene solutions